

FLAMMABILITY LIMITS OF LITHIUM-ION BATTERY THERMAL RUNAWAY  
VENT GAS IN AIR AND THE INERTING EFFECTS OF HALON 1301

By

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## ABSTRACT OF THE THESIS

### Flammability Limits of Lithium-Ion Battery Thermal Runaway Vent Gas in Air and the Inerting Effects of Halon 1301

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Lithium-ion (rechargeable) and lithium-metal (non-rechargeable) battery cells put aircraft at risk of igniting and fueling fires. Lithium batteries can be packed in bulk and shipped in the cargo holds of freighter aircraft; currently lithium batteries are banned from bulk shipment on passenger aircraft [1].

The federally regulated Class C cargo compartment extinguishing system's utilization of a 5 %vol Halon 1301 knockdown concentration and a sustained 3 %vol Halon 1301 may not be sufficient at inerting lithium-ion battery vent gas and air mixtures [2]. At 5 %vol Halon 1301 the flammability limits of lithium-ion premixed battery vent gas (Li-Ion pBVG) in air range from 13.80 %vol to 26.07 %vol Li-Ion pBVG. Testing suggests that 8.59 %vol Halon 1301 is required to render all ratios of the Li-Ion pBVG in air inert.

The lower flammability limit (LFL) and upper flammability limit (UFL) of hydrogen and air mixtures are 4.95 %vol and 76.52 %vol hydrogen, respectively. With the addition of 10 %vol and 20 %vol Halon 1301 the LFL is 9.02 %vol and 11.55 %vol hydrogen, respectively, and the UFL is 45.70 %vol and 28.39 %vol hydrogen, respectively. The minimum inerting concentration (MIC) of Halon 1301 in hydrogen and air mixtures is 26.72 %vol Halon 1301 at 16.2 %vol hydrogen.

The LFL and UFL of Li-Ion pBVG and air mixtures are 7.88 %vol and 37.14 %vol Li-Ion pBVG, respectively. With the addition of 5 %vol, 7 %vol, and 8 %vol Halon 1301 the LFL is 13.80 %vol, 16.15 %vol, and 17.62 % vol Li-Ion pBVG, respectively, and the UFL is 26.07 %vol, 23.31 %vol, and 21.84 %vol Li-Ion pBVG, respectively. The MIC of Halon 1301 in Li-Ion pBVG and air mixtures is 8.59 %vol Halon 1301 at 19.52 %vol Li-Ion pBVG.

Le Chatelier's mixing rule has been shown to be an effective measure for estimating the flammability limits of Li-Ion pBVGes. The LFL has a 1.79 % difference while the UFL has a 4.53 % difference. The state of charge (SOC) affects the flammability limits in an apparent parabolic manner, where the widest flammability limits are at or near 100 % SOC.

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## ABBREVIATIONS

Full Title	Abbreviation
Lithium-ion premixed battery vent gas.....	Li-Ion pBVG
Lithium-ion battery vent gas .....	Li-Ion BVG
Lower flammability limit .....	LFL
Minimum inerting concentration.....	MIC
State of charge .....	SOC
Upper flammability limit .....	UFL

## **Chapter I**

### **Introduction**

#### **1.1 Motivations**

Lithium-ion (rechargeable) and lithium-metal (non-rechargeable) battery cells put aircraft at risk of continual combustion or a possible explosion. Battery cells can self-ignite under a process called thermal runaway. This occurs through misuse, mishandling, or defective manufacturing. Thermal runaway in lithium batteries is associated with a rapid increase of temperature and the release of a toxic flammable gas.

Rechargeable and non-rechargeable lithium battery cells put aircraft at risk of igniting and fueling fires. Lithium batteries can be packed in bulk and shipped in the cargo holds of freighter aircraft; currently lithium batteries are banned from bulk shipment on passenger aircraft [1]. There have been high profile incidences involving aircraft carrying cargo of lithium batteries [3].

On February 7, 2006, an inflight fire on a UPS DC-8 forced an emergency landing in Philadelphia where the aircraft was destroyed on the ground [3]. On September 3, 2010, a severe inflight fire caused an UPS Boeing 747 to crash in Dubai where both crew members were killed [3]. On July 27, 2011, a severe inflight fire caused an Asiana Boeing 747 to crash 130 km west of Jeju Airport, South Korea, killing both crew members [3]. It is known that each of these aircraft carried bulk lithium batteries as cargo [3]. However, due to the

destructive nature of aircraft fires, it is difficult to determine the extent that lithium batteries had in these tragedies.

Extensive testing were conducted at the Federal Aviation Administration William J. Hughes Technical Center in Atlantic City, New Jersey to determine the vent gas constituents of 18650-sized (18 mm diameter and 650 mm length) lithium cobalt oxide ( $\text{LiCoO}_2$ ) rechargeable lithium-ion batteries at various states of charge [4]. The two main flammable gas constituents were found to be carbon monoxide ( $\text{CO}$ ) and hydrogen ( $\text{H}_2$ ) [4]. Experimental data has shown that increasing the state of charge (SOC) increases the overall volume of the vent gas and changes the vent gas composition [4].

The Federal Aviation Administration (FAA) cargo compartment requirements vary by the classification of the cargo compartment [5]. Cargo compartments can be classified as Class A, B, C, or E [5]. These cargo compartments are regulated by title 14 Code of Federal Regulations (CRF) part 25 §25.857 and is provided in appendix A-1 [5].

Class C fire protection is dependent on early fire detection and a built-in fire suppression system capable of releasing an initial knockdown concentration of 5 %vol Halon 1301 and sustaining 3 %vol Halon 1301 for the duration of the flight [2]. Additionally, there are fire resistant liners and a cockpit controlled compartment ventilation system [5]. This helps maintain proper concentrations of the extinguishing agent and keep hazardous wastes from occupied areas [5]. These Halon 1301 concentrations have been shown to be

effective for typical cargo fires [2]. However, adequacy concerns of the Halon 1301 concentrations for the shipment of lithium batteries have been raised [6].

## **1.2 Definition of Flammability Limits**

Fuel and oxidizer mixtures have a range of ratios in which the mixture is considered flammable. The lower flammability limit (LFL) is the minimum concentration of a fuel in an oxidizer that will ignite. This means that less fuel will render the mixture too lean to ignite. The upper flammability limit (UFL) is the maximum concentration of a fuel in an oxidizer that will ignite. This means that more fuel will render the mixture too rich to ignite.

## **1.3 Definition of Minimum Inerting Concentration**

As the concentration of an inert gas is increased, the flammability limits of the fuel and oxidizer mixture constrict until the LFL and UFL merge to a single point called the minimum inerting concentration (MIC). The MIC is the minimum concentration of an inert gas required to prevent the ignition of any ratio of fuel in an oxidizer.

## **1.4 Objectives**

The objective of this work is to determine if the 5 %vol knockdown and the 3 %vol sustained of Halon 1301 in a Class C cargo compartment are sufficient to render the buildup of a lithium-ion battery vent gas (Li-Ion BVG) in air inert. This is accomplished by experimentally determining the flammability limits

of lithium-ion premixed battery vent gas (Li-Ion pBVG) and air mixtures with varying concentrations of Halon 1301 and by determining the MIC of Halon 1301 on Li-Ion pBVG and air mixtures in a 21.7 liter pressure vessel.

The flammability limits of hydrogen and air have been extensively researched. The LFL and UFL of hydrogen and air mixtures are experimentally determined for testing validation. Then the LFL and UFL with 10 %vol and 20 %vol Halon 1301 and the MIC of Halon 1301 on hydrogen in air mixtures are determined.

The LFL and the UFL of a Li-Ion pBVG and air is determined without Halon 1301 and with 5 %vol, 7 %vol, and 8 %vol Halon 1301. The MIC of Halon 1301 on Li-Ion pBVG and air mixtures is also experimentally determined.

Flammability limits of gaseous mixtures can be theoretically calculated using Le Chatelier's mixing rule [7]. This is applied to the constituents of the LI-Ion pBVG and air. Then, the theoretical data is compared to the experimental data to determine if Le Chatelier's mixing rule is a viable option for predicting the flammability limits of other Li-Ion BVGeS and air.



## **Chapter II**

### **Background**

#### **2.1 Dependences of Flammability Limits**

It is possible to conduct experiments with accurate and reproducible data in a controlled environment. However, the application of flammability limits should be applied carefully while considering all possible variables. Some factors that affect the flammability limits are spark energy, ambient temperature, pressure, and vessel size [8].

##### **2.1.1 Flammability Limits vs. Spark Energy**

The flammability limits may be wider than what is experimentally determined. Due to lack of ignition strength, the experimentally determined flammability limits may be the ignitability limits rather than the real flammability limits [8]. The ignitability limits are similar to the flammability limits, as they are the range of fuel and oxidizer ratios considered flammable [8]. However the ignitability limits are dependent on the ignition source strength [8]. As the ignition strength increases, the ignitability limits expand [8]. When increasing the ignition source ceases to increase the ignitability limits, the real flammability limits are found [8]. Note that significantly more energy is required to find the UFL than the LFL [8] (Figure 2.1).

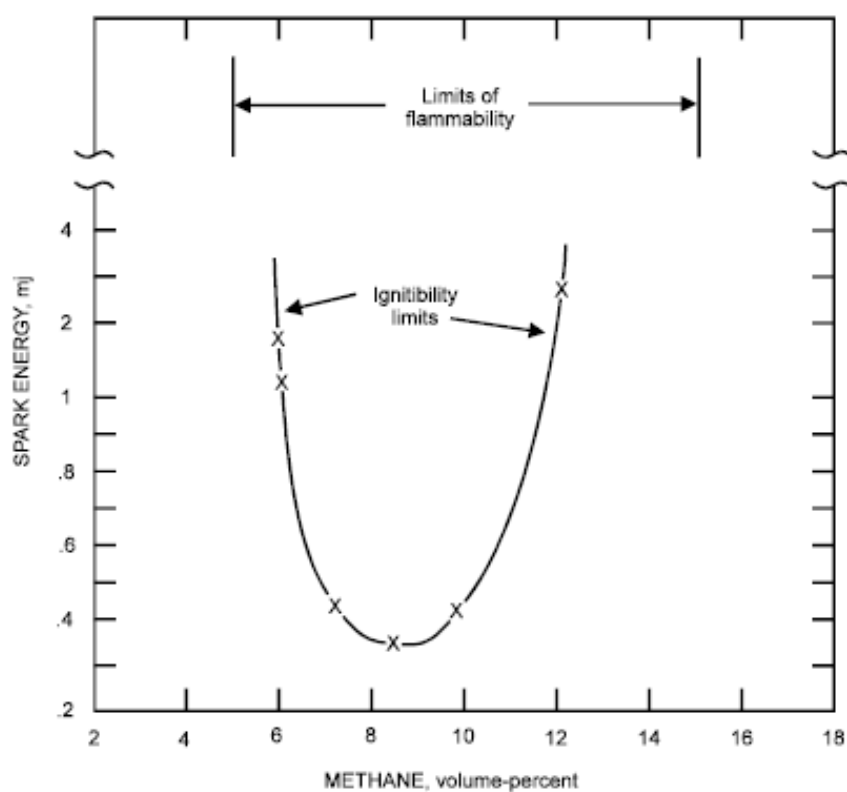


Figure 2.1: Ignitability curve and the flammability limits of methane and air mixtures [8]

### 2.1.2 Flammability Limits vs. Temperature

Small variations of temperature in a climate controlled lab show little to no variations in the flammability limits of lab results. However, the flammability limits are dependent on larger fluctuations of external temperature [8]. An increase in external temperature expands the flammability limits [8]. Equations to estimate the LFL and the UFL as a function of temperature can be derived using properties of paraffin hydrocarbons [8] (Equation 2.1 and 2.2).

$$\frac{L_t}{L_{25^\circ}} = 1 - 0.000784(t - 25^\circ)$$

Equation 2.1

$$\frac{U_t}{U_{25^\circ}} = 1 + 0.000721(t - 25^\circ)$$

Equation 2.2

Where  $L_{25^\circ}$  and  $U_{25^\circ}$  are the LFL and UFL at 25 °C and  $L_t$  and  $U_t$  are the LFL and UFL at the assigned temperature value  $t$ .

Stacks of lithium-ion batteries in thermal runaway have been shown to reach a peak temperature of 908 °C and stacks of lithium-metal batteries have been shown to reach a peak temperature of 1098 °C [6]. These extremely high temperatures can expand the flammability limits.

### **2.1.3 Flammability Limits vs. Pressure**

Small variations of pressure yield little to no difference in the flammability limits of lab results. However, estimating the flammability limits over larger variations in pressure is more difficult [7]. That is because changes in flammability limits are not constant and are specific to each particular mixture [7]. Experiments were conducted with hydrogen and air mixtures at simulated altitudes ranging from 0 feet to 40,000 feet [9]. It was determined that a decrease in pressure, over the previously mentioned range of simulated altitude, causes a decrease in the LFL and an increase in the UFL [9]. In other words, as the pressure decreases the flammability limits expand.

### **2.1.4 Flammability Limits vs. Pressure Vessel Size**

The size of the pressure vessel affects the experimental flammability limits [10]. Experiments were conducted to determine the LFL of hydrogen and air mixtures in pressure vessels of various sizes [10]. Tests were conducted in an 8 liter, 20 liter, 120 liter, and a 25,500 liter pressure vessel and found the LFL to be approximately 5 %vol, 6 %vol, 6.5 %vol, and 7.5 %vol hydrogen, respectively [10]. This yields a 50 % increase of the LFL simply by varying the vessel size, thus demonstrating the significance of using the flammability limits with caution in engineering applications.

## **2.2 Common Test Methods**

The complexities involved in determining the flammability limits of gases and vapors create the need for multiple testing methods. Two common test methods for determining flammability limits are visual inspection of flame propagation in a clear cylindrical tube, known as the visual method, and the other is measurement of overpressure inside a pseudo spherical vessel, known as the overpressure method. These two methods and variations within these methods can result in conflicting data. The European Standard cites up to 10 % difference in the measured flammability limits between the visual method and the overpressure method [11]. Therefore, to obtain reproducible and applicable data, it is imperative that a test method is clearly described and followed.

### **2.2.1 U.S. Bureau of Mines**

The Bureau of Mines Bulletin 503 describes the visual method. The Bureau of Mines Apparatus consists of a test tube with a 5 cm inside diameter and 150 cm length [7]. The ignition source is a spark gap igniter at the base of the tube [7]. The gases and vapors are considered flammable when the self-propagation of a flame is possible [7]. The flammability limits are determined by finding the mixture ratio in between flammable and non-flammable [7]. The LFL is determined by averaging the fuel concentrations of the largest nonflammable mixture and the smallest flammable mixture (equation 2.3) [7]. Similarly, the UFL is discovered by averaging the fuel concentrations of the largest flammable mixture and the smallest nonflammable mixture (equation 2.4) [7].

$$L_{T,P} = \frac{1}{2}(C_{gn} + C_{lf})$$

Equation 2.3

$$U_{T,P} = \frac{1}{2}(C_{gf} + C_{ln})$$

Equation 2.4

Where  $L_{T,P}$  and  $U_{T,P}$  are the lower and upper flammability limits [7].  $C_{gn}$  and  $C_{ln}$  are the largest and smallest concentration of flammable gases and vapors in an oxidizer that are considered nonflammable [7]. Similarly,  $C_{gf}$  and  $C_{lf}$  are the largest and smallest concentration of flammable gases and vapors in an oxidizer that are considered flammable [7].

### 2.2.2 ASTM International

The ASTM uses both the visual and the overpressure method. The visual method is described in Designation: E681 and the overpressure method is described in Designation: E2079.

Designation: E681 describes the visual method where the test apparatus consists of a 5 liter glass flask [12]. The spark igniter consists of a 1 mm L-shaped tungsten or platinum wire, separated by 6.4 mm at a distance of 1/3 diameter from the bottom of the flask [12]. The power supply is approximately 30 mA at 15 kV and the spark time is between 0.2 and 0.4 seconds [12]. The gases and vapors are considered flammable when flame propagation is visually observed [12]. The ASTM defines propagation of flame as an upward and outward movement of the flame front from the ignition source to within 13 mm of

the vessel's wall [12]. Similar equations to the U.S. Bureau of Mines, equations 2.3 and 2.4, are used to determine the flammability limits.

The overpressure method is described in Designation: E2079 where the test apparatus consists of a pseudo spherical test vessel with a volume of at least 4 liters and a maximum of 35 liters [13]. The various accepted ignition sources are fuse wire, carbon spark, continuous electric arc, discrete electric spark, and chemical igniter [13]. All of which must have the ignition point located near the center of the vessel [13]. The steel or graphite electrodes are placed 6 mm apart with a spark lasting less than 1 second [13]. A 30 mA, 115/15 kV luminous tube transformer is recommended [13]. An overpressure greater than or equal to 7% over the initial absolute test pressure is the criterion used to consider gases and vapors flammable [13].

### **2.2.3 European Standard**

The European Standard EN 1839 implements both the visual method and the overpressure method. The visual method is labeled as method T and the overpressure method is labeled as method B.

The visual method test apparatus consists of an upright cylindrical vessel made of glass or another transparent material, the inside diameter is  $80 \pm 2$  mm and has a minimum length of 300 mm [11]. The ignition source is a series of induction sparks between two stainless steel electrodes which are placed  $60 \pm 1$  mm above the bottom of the test vessel with the tips at a distance of  $5 \pm 0.1$  mm at angle of  $60 \pm 3$  degrees [11]. The power supply is between 20 mA to 30 mA at 13

kV to 16 kV with a spark time between 0.2 and 0.5 seconds [11]. The spark power at standard atmospheric condition is approximately 10 W [11]. The gases are considered flammable when there is self-propagating combustion, meaning there is upward movement of the flame from the spark gap for at least 100 mm [11]. The LFL is determined by testing for five consecutive nonflammable mixtures with the largest concentration of flammable gases, just before a flammable mixture is reached [11]. Similarly, the UFL is determined by testing for five consecutive nonflammable mixtures with the smallest concentration of flammable gases, just before a flammable mixture is reached [11]. Rather than using the average of the five tests, the lowest and the highest nonflammable mixture is used in determining the LFL and the UFL, respectively [11].

The overpressure method test apparatus is at least 5 liters [11]. The same ignition source guidelines outlined above in the European Standard visual method applies, with the only difference being the electrodes are placed at the center of the vessel [11]. An overpressure greater than or equal to  $5 \pm 0.1$  % over the initial test pressure plus the overpressure caused by the ignition source in air is the criterion used to consider gases and vapors flammable [11]. The same standard for determining the flammability limit outlined above in the European Standard visual method is used for the European Standard overpressure method [11].

### **2.3 Lithium Battery Thermal Runaway Vent Gas Constituents by Charge**

Extensive testing was conducted at the Federal Aviation Administration William J. Hughes Technical Center in Atlantic City to determine



the vent gas constituents of 18650-sized  $\text{LiCoO}_2$  rechargeable lithium-ion battery cells at various states of charge [4]. The three main constituents were found to be carbon monoxide ( $\text{CO}$ ), carbon dioxide ( $\text{CO}_2$ ), and hydrogen ( $\text{H}_2$ ) (Figure 2.2) [4]. The remaining constituents are various hydrocarbons. It was found that increasing the SOC increases the overall lithium battery vent gas volume and changes the lithium battery vent gas composition (Figure 2.2 and 2.3).

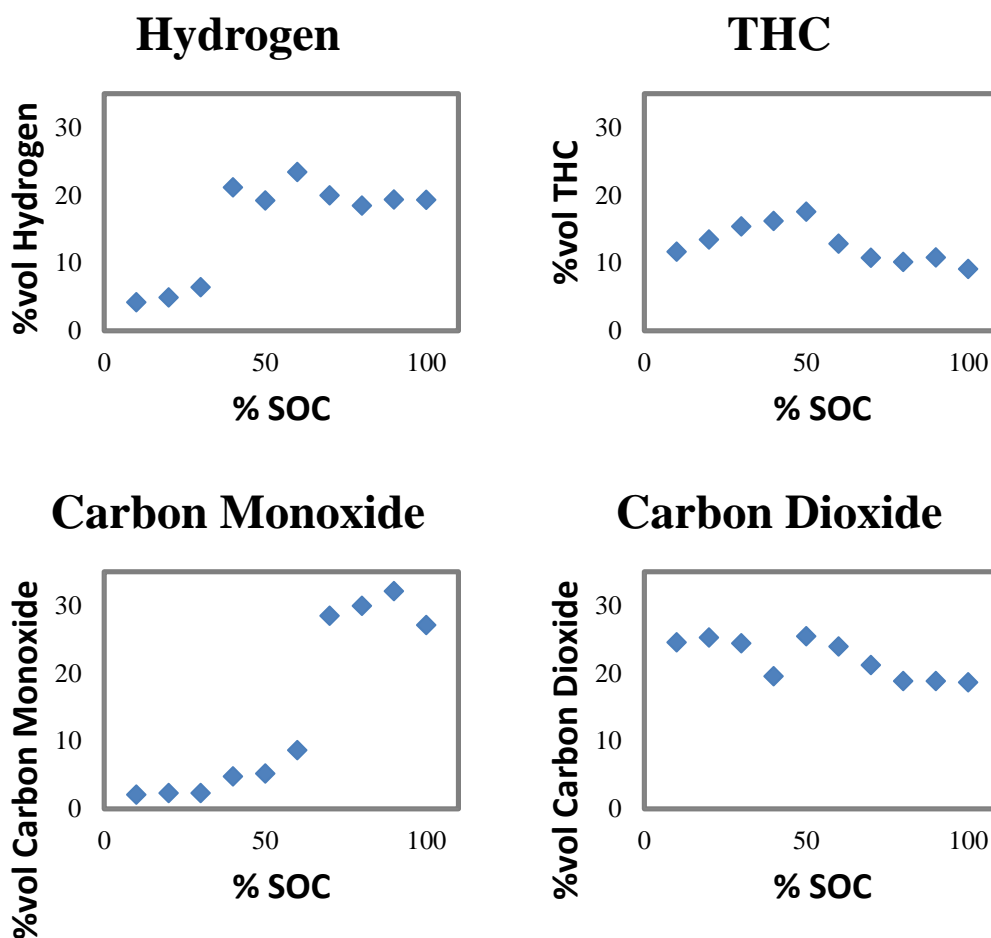


Figure 2.2: Major gas species concentrations for 18650-sized  $\text{LiCoO}_2$  rechargeable lithium-ion cells

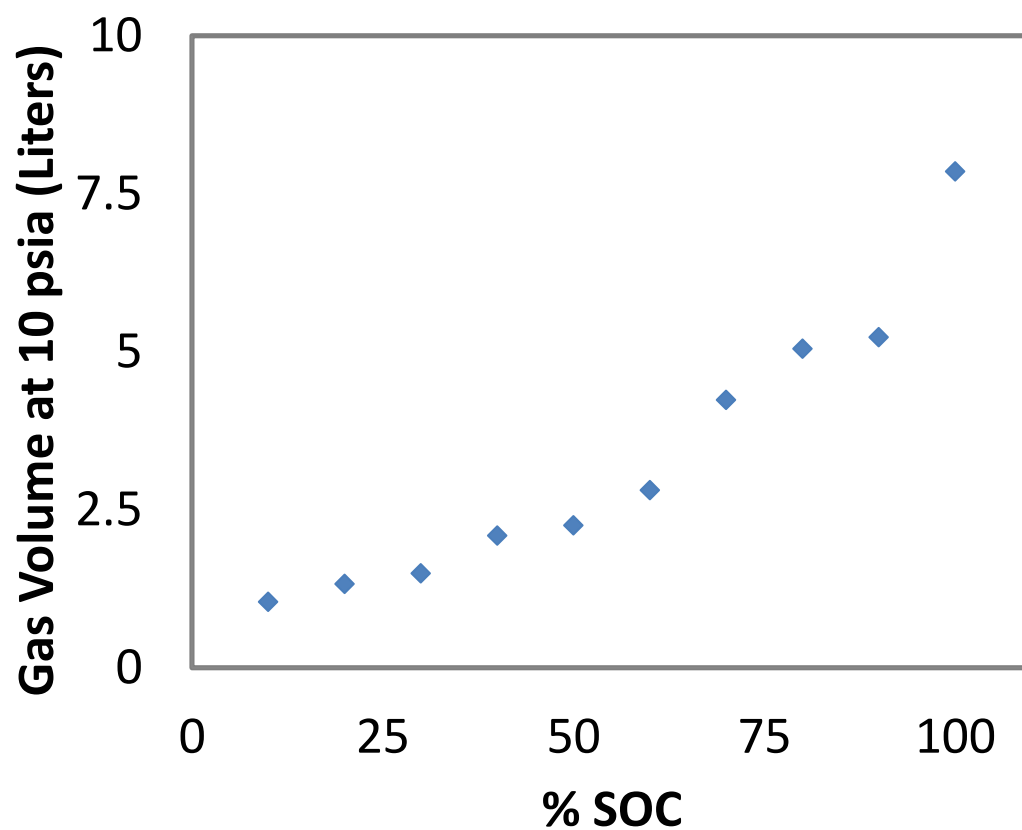


Figure 2.3: Gas volume emitted from 18650-sized LiCoO<sub>2</sub> rechargeable lithium-ion cells

## **Chapter III**

### **Flammability Apparatus and Experimental Method**

The test method of choice for the Federal Aviation Administration Technical Center testing facilities is the overpressure method. An overpressure greater than or equal to 5 % over the initial test pressure plus the averaged overpressure caused by the ignition source at ambient temperature and pressure in air is used to determine gases and vapors flammable.

Five tests were conducted and averaged to determine the overpressure caused by the ignition source in air. At 14.7 psi the tested ignition source averaged an overpressure of 0.0164 psi with a standard deviation of 0.00134 psi.

The flammability limits are determined in three steps:

1. Increase or decrease the fuel concentration by ~ 0.05 %vol intervals until a nonflammable mixture is tested.
2. Test five nonflammable mixtures within ~ 0.05 %vol of one another to determine flammability limit.
3. Average five nonflammable results.

#### **3.1 Testing Vessel**

Experiments were conducted in a 21.7 liter stainless steel pressure vessel based on the Bureau of Mines 20 liter explosibility chamber for dusts [14].

The vessel is semi-spherical and is made of 316 L stainless steel. The wall thickness is 13 mm with an outside diameter of 323.85 mm. The hinged head is secured with 6 stainless steel hex head 3/4 - 10 X 4.25" bolts and is sealed with a rubber O-ring. The pressure vessel has multiple ports for pressure transducers, gas lines, igniters, a mixing fan, and a thermocouple (Figure 3.1).

The pressure vessel was hydrostatically leak checked in accordance with ASTM E1003 – 13 [15]. Testing was conducted by Laboratory Testing Inc. in Hatfield, PA, where the pressure vessel was pressurized with water to 300 psi for 15 minutes. The pressure vessel passed the hydrostatic leak check with a leakage rate of less than  $4.5 \times 10^{-7}$  mol/s. The leak check is essential for testing safety and mitigates risks involved in flammability testing.

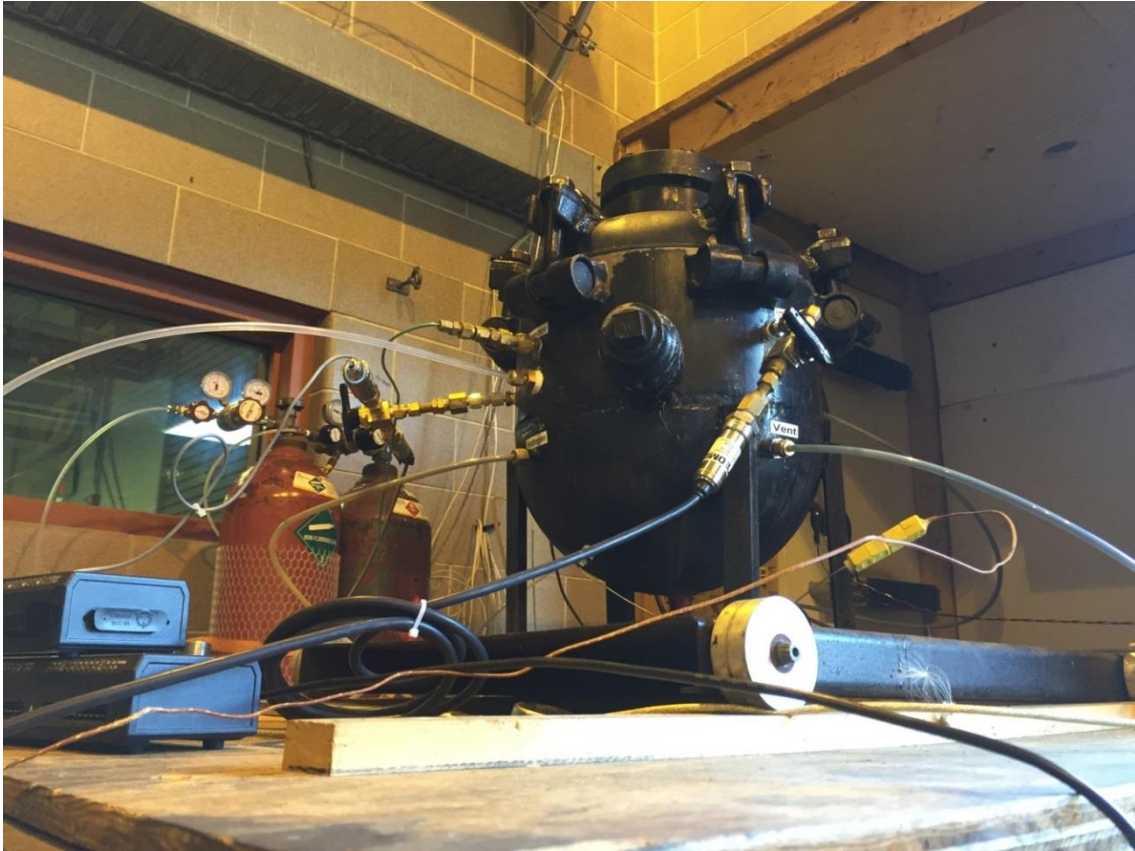


Figure 3.1: Testing Pressure Vessel

### 3.2 Ignition Background

As noted in section 2.2.1 Flammability Limit vs. Spark Energy, the amount of spark energy can affect test results. If there is not enough spark energy being supplied, the measured limits may be the ignitability limits rather than flammability limits (Figure 2.1).

Just as it is possible to not have enough energy, it is possible to have too much energy for a given test vessel. If the igniter spark energy is too large for the size of the test vessel, the spark can ground out to the test vessel and reduce the reproducibility of the test data. Furthermore, it is also possible for

burning dust to yield false positive flammable results with too high of high spark energy [16].

### **3.2.1 Ignition Equipment**

The 15 kV, 30mA luminous tube transformer (Allanson 1530BPX120) was selected as the power source based on the recommendation of three ASTM designations: E681-09 Standard Test Method For Concentration Limits of Flammability of Chemicals (Vapors and Gases), E1515-07 Standard Test Method for Minimum Explosible Concentration of Combustible Dusts, E2079-07 Standard Test Methods for Limiting Oxygen (Oxidant) Concentration in Gases and Vapors, and the European Standard EN1839 Determination of Explosion Limits of Gases and Vapours [11][12][13][16]. Two 3.2 mm diameter 316L stainless steel electrodes were chosen based on the recommendation of ASTM E2079 and the European Standard EN1839 [11][13].

### **3.2.2 Ignition Equipment Testing**

After the transformer and electrodes are chosen, the only variables affecting the spark energy are the electrode gap distance and spark time. Testing was conducted to maximize the effectiveness of the ignition equipment, with the goal of maximizing spark energy and reproducibility.

The test equipment consists of a high voltage probe (Tektronix P6015A) and a current probe (Tektronix A621), which connects to a digital oscilloscope (Tektronix THS 730A) and a computer to record data at 12.5 kHz

per channel. The test equipment is capable of recording voltage and current.

Using the recorded voltage and current, the spark power and spark energy can be calculated.

The voltage and current were measured for 10 tests at 5 different gap distances at standard atmospheric pressure and temperature with a spark time of 0.5 seconds. The tested gap distances are 6.4 mm, 10.2 mm, 12.7 mm, 16.5 mm, and 19 mm. For each of the tests, the spark energy is calculated. Then for each gap distance, the spark energies are averaged and the standard deviation is calculated (Table 3.1). As the spark gap increases, there is a gradual increase in spark energy up until the gap distance of 19 mm. At this point, the spark energy decreases. This is because the large gap caused the spark to ground out to the test vessel.

Gap Distance, mm	Spark Energy, J	Standard Deviation, J
6.4	11.74	0.1765
10.2	13.06	0.4285
12.7	16.30	0.7043
16.5	17.92	0.8247
19.0	17.44	1.4826

Table 3.1: Tabulated gap distance, spark energy, and standard deviation of 10 averaged tests. Tests were conducted at atmospheric pressure and 25° C.

### 3.2.3 Ignition Equipment Setup

The ASTM and European Standard recommend various spark gap distances. The ASTM recommends a distance of 6.4 mm in Designation: E681 and 6 mm in Designation: E2709, while the European Standard recommends a distance of  $5 \pm 0.1$  mm at an angle of  $60 \pm 3^\circ$  [11] [12] [13]. However, the gap

distance of 16.5 mm was selected because it produces the largest spark energy while maintaining its consistency. The gap distance of 16.5 mm averaged energy above the slope of linear regression and the standard deviation is below the slope of linear regression, thus yielding the most reproducible spark with the highest energy (Figure 3.2).

The ASTM recommends a spark time between 0.2 and 0.4 seconds in Designation: E681 and a spark time of less than 1 second in Designation: E2709, the European Standard recommends a spark time between 0.2 and 0.5 seconds [11][12][13]. Based on the spark tests and recommendations, a spark time of 0.5 seconds will be used.

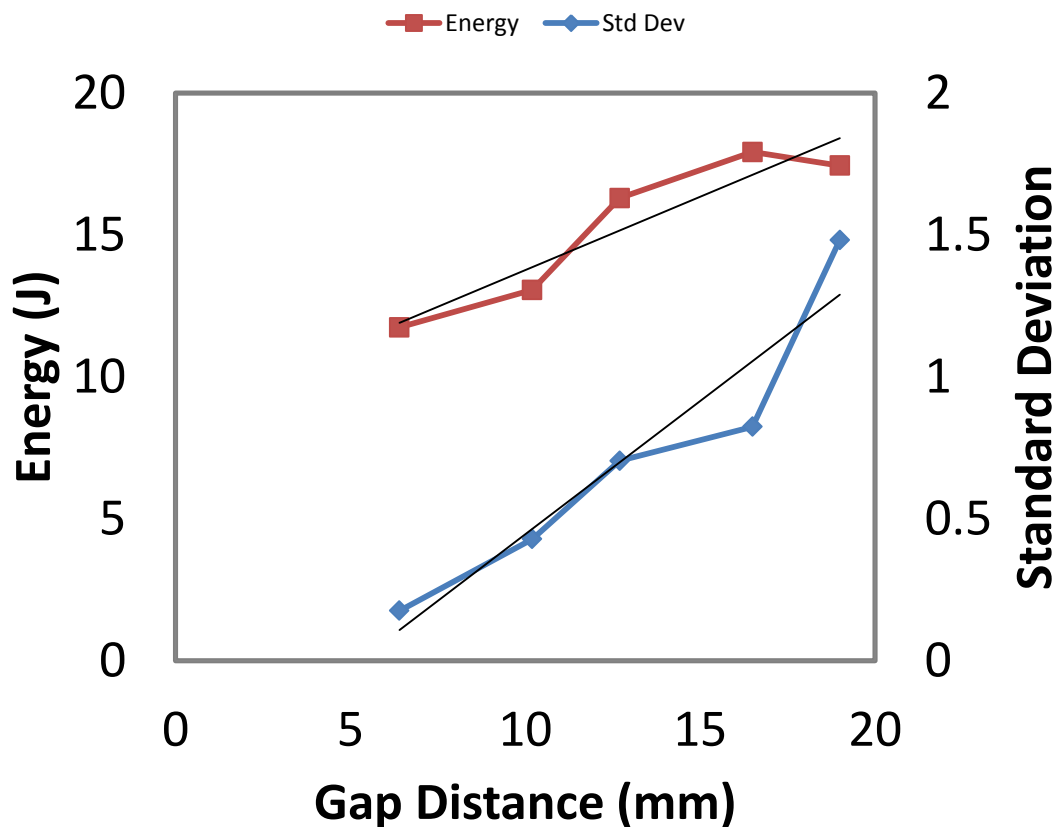


Figure 3.2: Spark energy and standard deviation of 10 averaged tests over various spark gap distances



### 3.3 Measurement Equipment

Pressure data is acquired using three pressure transducers, one high pressure transducer with a range from 0-150 psi (Omega MMA150V5P3C1T4A5S) and two low pressure transducers, one with a range from 0-15 psi (Omega MMA015V5P3C1T3A5S) and the other with a range from 0-30 psi (Omega PX329-030A5V). The high pressure transducer is used to acquire pressure data outside the range of the two low pressure transducers. The 0-15 psi pressure transducer is used for inputting partial pressures and the 0-30 psi pressure transducer is used to acquire data near the flammability limits. A thermocouple (Omega KQCL 1/16") is used to measure the initial ambient temperature.

The 0-15 psi pressure transducer and the thermocouple are connected to a low speed data acquisition system (IOtech Personal Daq/56 with PDQ2) and the 0-30 psi and the 0-150 psi pressure transducers are connected to a high speed data acquisition system (Omega OMB-DAQ-3000) to collect data at 1 kHz.

### 3.4 Bottles and Miscellaneous Equipment

A 12 V CPU cooling fan is placed at the bottom of the testing vessel facing upward and at a slight angle for optimal mixing.

Bottled hydrogen (Praxair HY 5.0UH-T), Li-Ion pBVG (Praxair NI BT1.58X1CASN), and air (Praxair AI 0.0UZ-T) are used for testing. The constituents of the Li-Ion pBVG are shown in table 3.2.

<b>Gas</b>	<b>%vol</b>
Hydrogen	27.60
Carbon Monoxide	22.90
Carbon Dioxide	30.10
Methane	6.37
Propylene	4.48
Ethylene	2.21
Butane	1.57
Ethane	1.17
1-Butane	0.56
Propane	0.27

Table 3.2: Constituents of lithium-ion premixed battery vent gas

## **Chapter IV**

### **Test Procedures**

Test procedures must be followed to acquire accurate and reproducible data. Test procedures are broken up into three parts. The first being startup procedures, which occur prior to testing. The second is testing procedures, which is where data is acquired. The last is shutdown procedures, which occurs at the end of testing.

#### **4.1 Startup Procedures**

1. Open valves to gas cylinders, solenoids, and pressure regulators.
2. Turn on 28 V circuit to power pressure transducers, mixing fan, and gas solenoid relays.
3. Turn on 115 V circuit to power the solenoids.
4. Start computer and data acquisition software.

#### **4.2 Testing Procedures**

1. Flush gas lines for 5 to 10 seconds to ensure purity of gases entering pressure vessel.
2. Flush pressure vessel with compressed air for a minimum of 15 minutes.
3. Evacuate test chamber by opening vacuum valve and turning vacuum pump on. Pressure is to be reduced to ~0.15 psi.

4. Open valve to low pressure transducer for partial pressure measurement of input gases.
5. Use partial pressure to input the required ratio of gases for testing. Insert gases one at a time by opening the solenoid associated with the respective gas. Adjust needle valve to control gas flow rate.
6. Turn on mixing fan for a minimum of 10 minutes to ensure proper mixing.
7. Close valve to low pressure transducer. This is done because pressure spikes above the pressure transducer's range may cause permanent damage to the pressure transducer's diaphragm.
8. Open valve to high speed pressure transducer corresponding to either the 0 – 30 psi pressure transducer for tests near the flammability limits or the 0 – 150 psi for tests well within flammability limits.
9. Turn off mixing fan for 1 minute prior to spark ignition to reduce turbulence.
10. Start recording pressure transducer data for at least 2 seconds prior to ignition to measure the initial temperature and pressure. Record the pressure at a rate of 1000 Hz to ensure an accurate reading of the pressure spike. Continue to record data for at least another 2 seconds after ignition so that the entire test is recorded.
11. An overpressure greater than or equal to 5 % over the initial test pressure plus the averaged overpressure caused by the ignition source in atmospheric pressure and ambient temperature in air will be used to consider gases and vapors flammable.

### **4.3 Shutdown Procedures**

1. Close valves to gas cylinders, solenoids, and pressure regulators.
2. Turn off 28 V.
3. Turn off 115 V circuit.
4. Save data and shutdown computer and data acquisition software.

## Chapter V

### Hydrogen Flammability in Air with and without Halon 1301 Addition

#### 5.1 Overview

Hydrogen is known to have wide flammability limits and is a major contributor to the constituents of Li-Ion BVGs, especially at a SOC at or above ~50 % (Figure 2.2). Therefore, an understanding of how hydrogen reacts in air can yield insight of how Li-Ion BVGs will react in air. This holds true with the addition of Halon 1301 as an inert gas.

The flammability limits of hydrogen and air mixtures have been well documented and studied. This allows for validation of test results.

#### 5.2 Experimental Results

Experimental flammability limits of hydrogen in air are determined without the addition of Halon 1301 and with the addition of 10 %vol and 20 % vol Halon 1301 (table 5.1). As the concentration of Halon 1301 increases the flammability limits constrict until they coincide at the MIC of 26.72 %vol Halon 1301 (table 5.2).

Mixture	LFL, %vol Hydrogen	UFL, %vol Hydrogen
Hydrogen – Air	4.95±0.40	76.52±0.44
Hydrogen – Air – 10 % Halon 1301	9.02±0.51	45.70±0.41
Hydrogen – Air – 20 % Halon 1301	11.55±0.48	28.39±0.47

Table 5.1: Flammability limits of hydrogen and air mixtures with and without Halon 1301 addition

<b>Mixture</b>	<b>MIC, %vol Halon 1301</b>
Hydrogen – Air – Halon 1301	26.72±0.43

Table 5.2: Halon 1301 minimum inerting concentration of hydrogen in air

### 5.2.1 Hydrogen Flammability in Air without Inert Gas

15 tests were conducted to determine that the LFL of hydrogen and air mixtures is  $4.95 \pm 0.40$  %vol hydrogen (Figure 5.1). 21 tests were conducted to determine that the UFL of hydrogen and air mixtures is  $76.52 \pm 0.44$  %vol hydrogen (Figure 5.2).

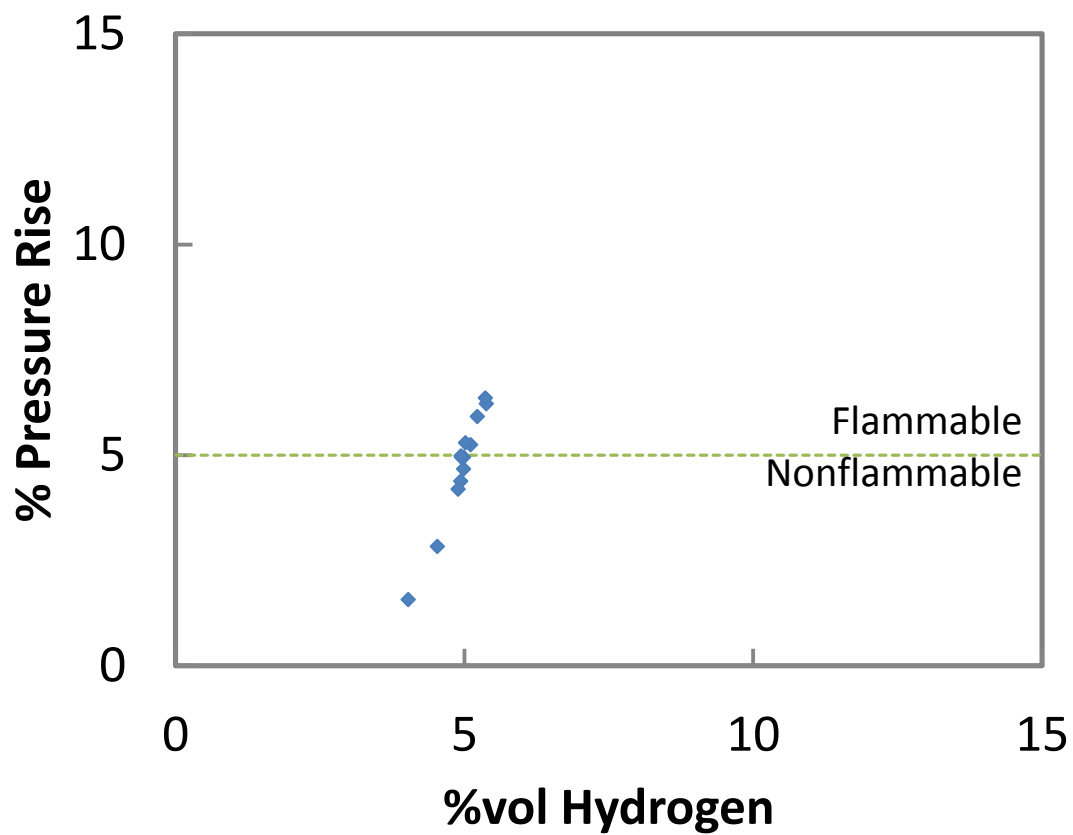


Figure 5.1: LFL of hydrogen in air



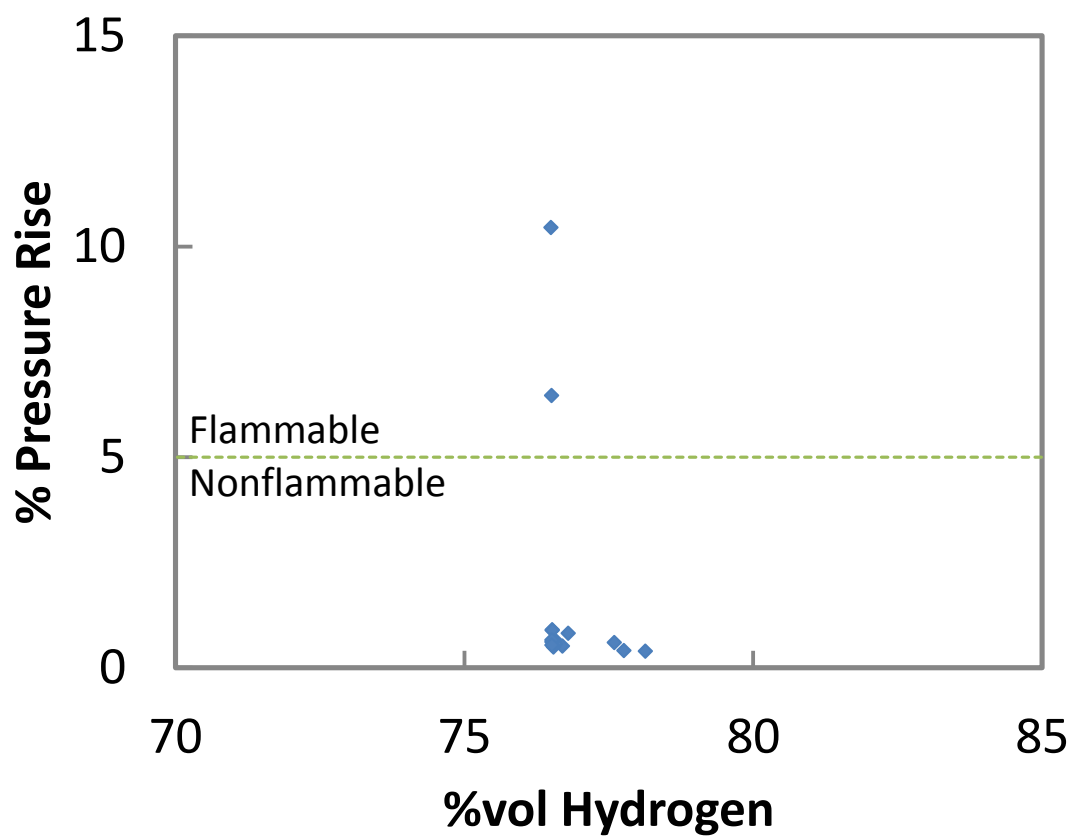


Figure 5.2: UFL of hydrogen in air

### **5.2.2 Hydrogen Flammability in Air with 10 % Halon 1301 by Volume**

#### **Addition**

13 tests were conducted to determine that the LFL of hydrogen, air, and 10 %vol Halon 1301 mixtures is  $9.02 \pm 0.51$  %vol hydrogen (Figure 5.3). 21 tests were conducted to determine that the UFL of hydrogen, air, and 10 %vol Halon 1301 mixtures is  $45.70 \pm 0.41$  %vol hydrogen (Figure 5.4).

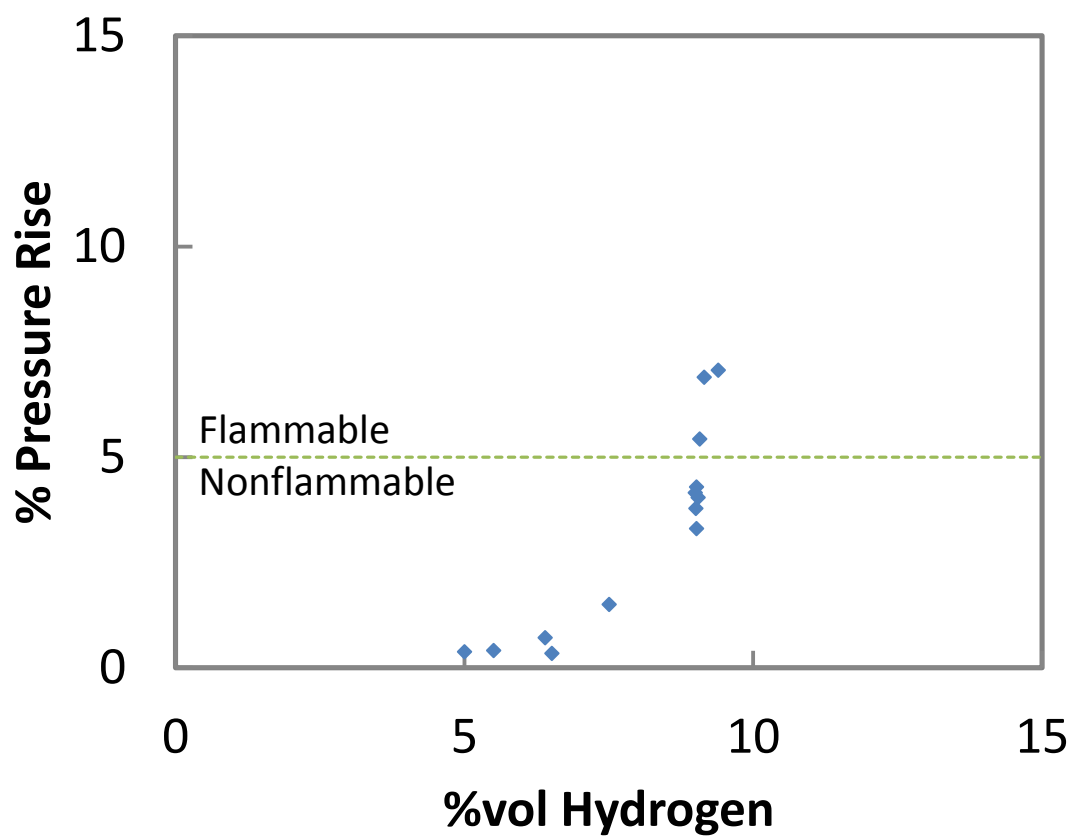


Figure 5.3: LFL of hydrogen in air with 10 % Halon 1301 by volume

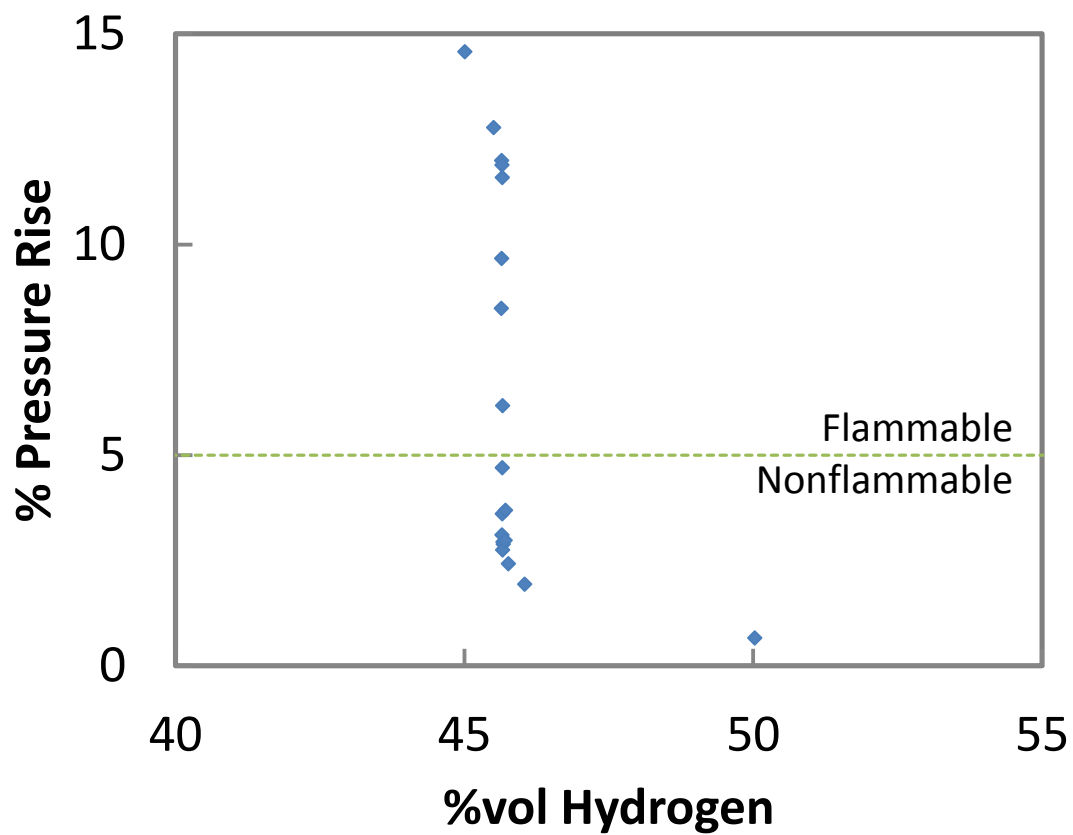


Figure 5.4: UFL of hydrogen in air with 10 % Halon 1301 by volume

### **5.2.3 Hydrogen Flammability in Air with 20 % Halon 1301 by Volume**

#### **Addition**

14 tests were conducted to determine that the LFL of hydrogen, air, and 20 %vol Halon 1301 mixtures is  $11.55 \pm 0.48$  %vol hydrogen (Figure 5.5). 16 tests were conducted to determine that the UFL of hydrogen, air, and 20 %vol Halon 1301 mixtures is  $28.39 \pm 0.47$  %vol hydrogen (Figure 5.6).

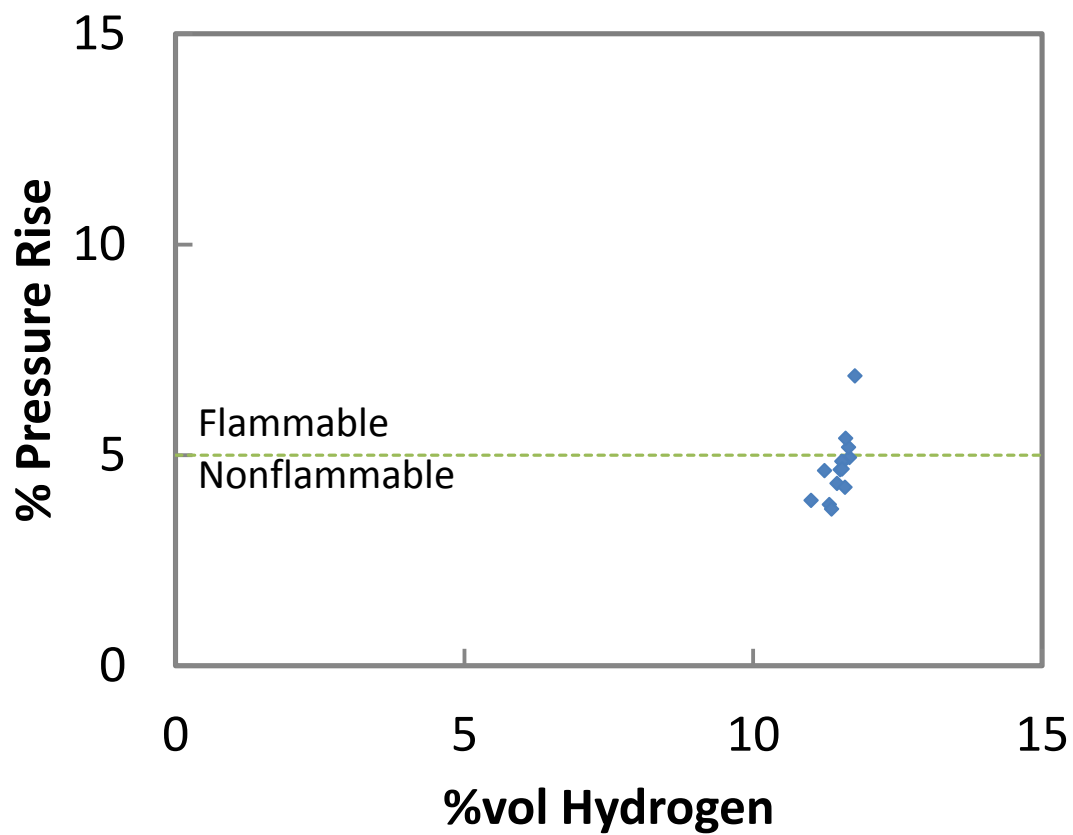


Figure 5.5: LFL of hydrogen in air with 20 % Halon 1301 by volume

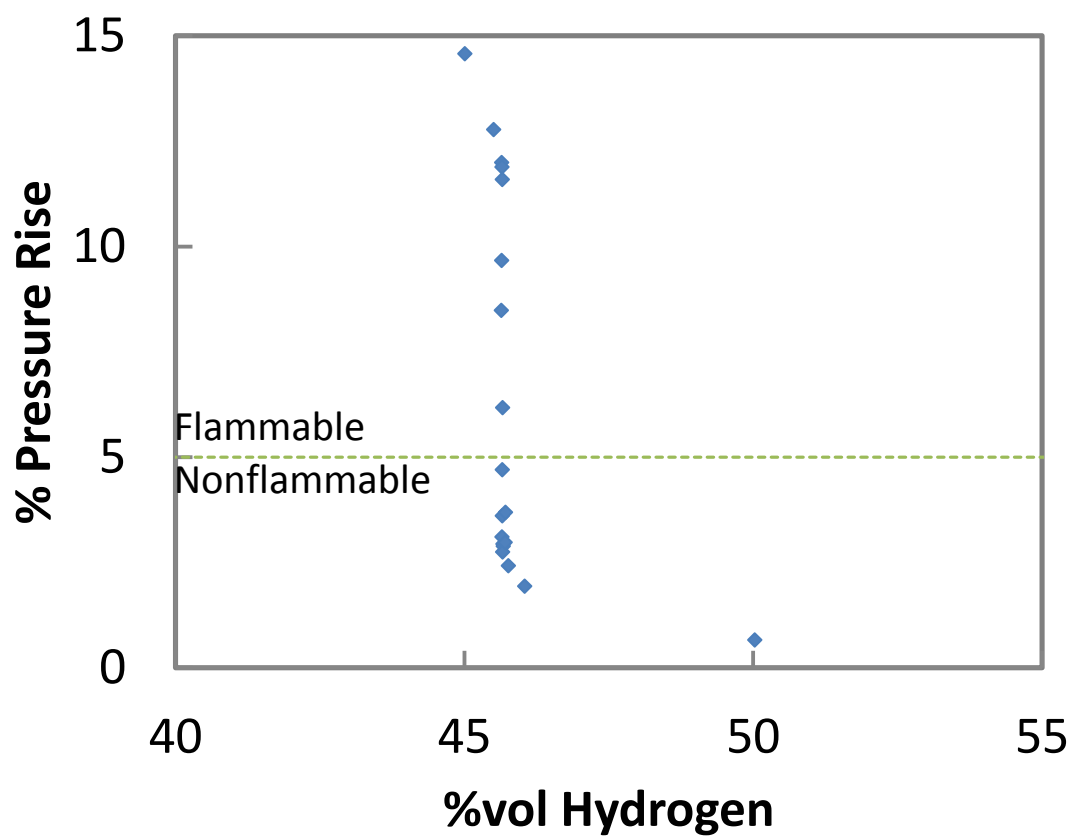


Figure 5.7: UFL of hydrogen in air with 20 % Halon 1301 by volume

#### **5.2.4 Halon 1301 Minimum Inerting Concentration of Hydrogen in Air**

21 tests were conducted to determine the minimum inerting concentration of Halon 1301 in hydrogen and air mixtures to be  $26.72 \pm 0.43$  %vol Halon 1301 at 16.2 %vol hydrogen (Figure 5.7).



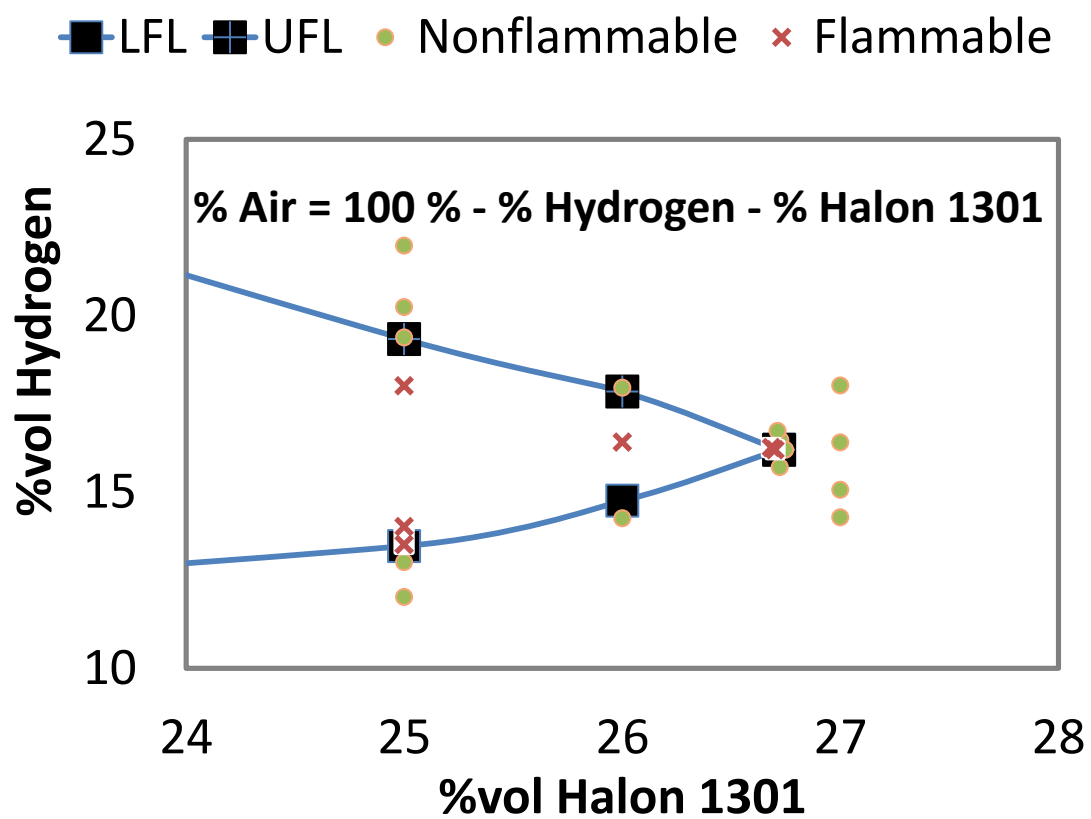


Figure 5.7: Flammability nose cap of hydrogen, air, and Halon 1301 mixtures

### 5.3 Testing Validation

Seven separate experiments determining the flammability limits of hydrogen and air are averaged together and the standard deviation is calculated. Five of the experiments used the pressure rise method and the other two used the visual method. It is found that the averaged LFL of seven experiments is 4.56 %vol hydrogen with a standard deviation of 0.54 %vol hydrogen, while the averaged UFL of seven experiments is 77.11 %vol hydrogen with a standard deviation of 0.88 %vol hydrogen (Table 5.3). The experimentally determined flammability limits of this study are  $4.95 \pm 0.40$  %vol and  $76.52 \pm 0.44$  %vol hydrogen for the LFL and UFL, respectively (Table 5.3). Both are within a standard deviation of the averaged results and therefore validate the test data.

Results of the MIC were compared to a study completed by Factory Mutual Research Corporation in 1975 and yielded similar results. Results from this study found a MIC of 26.72 %vol Halon 1301 while Factory Mutual Corporation found the MIC to be 28 %vol Halon 1301 yielding a 4.68 % difference (Table 5.4) [18]. Being that the Factory Mutual Research Corporation used the visual method and this study used the pressure rise method, these results are within reason of uncertainty [18].

<b>Tester</b>	<b>LFL, %vol Hydrogen</b>	<b>UFL, %vol Hydrogen</b>
Matthew Karp with Mixing Fan (5 % pressure rise)	4.95±0.40	76.52±0.44
Matthew Karp without Mixing Fan (5 % pressure rise)	5.35	78.18
Steve Rehn without Mixing Fan (3 % Pressure Rise) [9]	4.7	78.87
Factory Mutual Research Corporation (Visual Upward Flame Propagation) [18]	4	76
EN 1839 (B) 14 L Vessel (5 % Pressure Rise) [17]	4.2	77
EN 1839 (T) 80 mm Diameter (Visual Method) [17]	3.6	76.6
Herzberg & Cashdollar 8 L Vessel (3 % Pressure Rise) [10]	5±0.5	76.8±0.2
Average	4.56	77.11

Table 5.3: Comparison of flammability limits of hydrogen and air mixtures

<b>Tester</b>	<b>MIC, %vol Halon 1301</b>
Matthew Karp with Mixing Fan (5 % Pressure Rise)	26.72±0.43
Factory Mutual Research Corporation (Visual Upward Flame Propagation) [18]	28

Table 5.4: Comparison of MIC of hydrogen, air, and Halon 1301 mixtures

## 5.4 Summary

15 tests were conducted to determine that the LFL of hydrogen and air mixtures is 4.95±0.40 %vol hydrogen (Figure 5.1). 21 tests were conducted to determine that the UFL of hydrogen and air mixtures is 76.52±0.42 %vol hydrogen (Figure 5.2).

13 tests were conducted to determine that the LFL of hydrogen, air, and 10 %vol Halon 1301 mixtures is 9.02±0.51 %vol hydrogen (Figure 5.3). 21

tests were conducted to determine that the UFL of hydrogen, air, and 10 %vol Halon 1301 mixtures is  $45.70 \pm 0.41$  %vol hydrogen (Figure 5.4).

14 tests were conducted to determine that the LFL of hydrogen, air, and 20 %vol Halon 1301 mixtures is  $11.55 \pm 0.48$  %vol hydrogen (Figure 5.5). 16 tests were conducted to determine that the UFL of hydrogen, air, and 20 %vol Halon 1301 mixtures is  $28.39 \pm 0.47$  %vol hydrogen (Figure 5.6).

21 tests were conducted to determine the minimum inerting concentration of Halon 1301 in hydrogen and air mixtures to be  $26.72 \pm 0.43$  %vol Halon 1301 at 16.2 %vol hydrogen (Figure 5.7).

All of the test results are graphed together to form the flammability curve of hydrogen, air, and Halon 1301 mixtures (Figure 5.8). The UFL constricts faster than the LFL as the %vol of Halon 1301 increases. Inside of the curve is considered flammable while outside the curve is considered nonflammable. Using the graph, any ratio of hydrogen, air, and Halon 1301 can be determined to be a flammable or nonflammable mixture. Hydrogen is a major contributor to the constituents of Li-Ion BVGes, especially at a SOC at or above ~50 % (Figure 2.2). Therefore, this flammability curve can yield insight of how Li-Ion BVGes will react in air.

It is found that the averaged LFL is 4.56 %vol hydrogen with a standard deviation of 0.54 %vol hydrogen, while the UFL is found to be 77.11 %vol hydrogen with a standard deviation of 0.88 %vol hydrogen (Table 5.3). The experimentally determined flammability limits of this study are  $4.95 \pm 0.40$  %vol

and  $76.52 \pm 0.44$  %vol hydrogen for the LFL and UFL, respectively (Table 5.3).

Both are within a standard deviation of the averaged results.

Results of the MIC were compared to a study completed by Factory Mutual Research Corporation in 1975 and yielded similar results. Results from this study found a MIC of 26.72 %vol Halon 1301 while Factory Mutual Corporation found the MIC to be 28 %vol Halon 1301 yielding a 4.68 % difference (Table 5.4) [18]. Being that the Factory Mutual Research Corporation used the visual method and this study used the pressure rise method, these results are within reason of uncertainty [18].

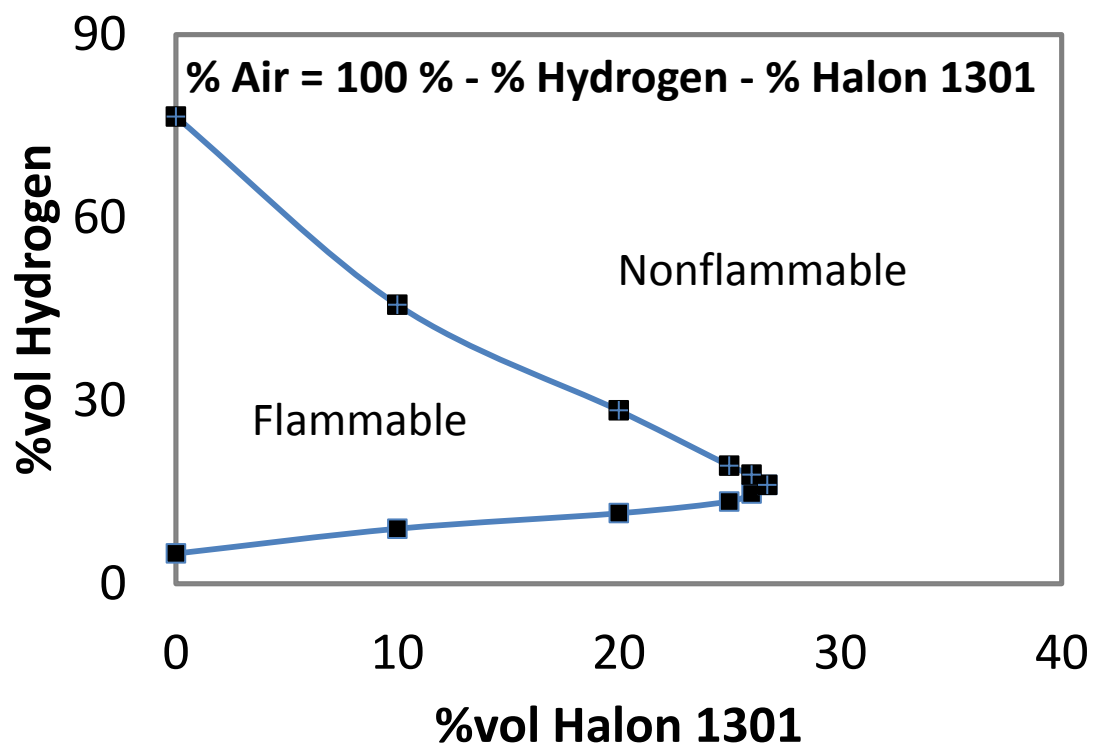


Figure 5.8: Flammability curve of hydrogen, air, and Halon 1301 mixtures

## **Chapter VI**

### **Lithium Battery Thermal Runaway Vent Gas Flammability in Air with and without Halon 1301 Addition**

#### **6.1 Overview**

Tests are conducted to determine if the 5 %vol knockdown and the 3 %vol sustained of Halon 1301 in a Class C cargo compartment are sufficient to render the buildup of a Li-Ion BVG in air inert. This is accomplished by experimentally determining the MIC of Halon 1301 on Li-Ion pBVG (table 3.2) and air mixtures; and by determining the flammability limits of Li-Ion pBVG and air mixtures with varying concentrations of Halon 1301 in a 21.7 liter pressure vessel.

The LFL and the UFL of Li-Ion pBVG and air are determined without Halon 1301, with 5 %vol, 7 %vol, and with 8 %vol Halon 1301. The MIC of Halon 1301 on Li-Ion pBVG and air mixtures is also experimentally determined.

## 6.2 Experimental Results

Experimental flammability limits of Li-Ion pBVG in air are determined without the addition of Halon 1301 and with the addition of 5 %vol, 7 %vol, and 8 %vol Halon 1301 (table 6.1). As the concentration of Halon 1301 increases the flammability limits constrict until they coincide at the MIC of 8.59 %vol Halon 1301 (table 6.2).

Mixture	LFL, %vol Hydrogen	UFL, %vol Hydrogen
Li-Ion pBVG – Air	7.88±0.41	37.14±0.42
Li-Ion pBVG – Air – 5% Halon 1301	13.80±0.49	26.07±0.43
Li-Ion pBVG – Air – 7% Halon 1301	16.15±0.4	23.31±0.44
Li-Ion pBVG – Air – 8% Halon 1301	17.62±0.52	21.84±0.65

Table 6.1: Flammability limits of lithium-ion premixed battery vent gas and air mixtures with and without Halon 1301 addition

Mixture	MIC, %vol Halon 1301
Li-Ion pBVG – Air – Halon 1301	8.59±0.52

Table 6.2: Halon 1301 minimum inerting concentration of lithium-ion premixed battery vent gas in air

### 6.2.1 Lithium-Ion Premixed Battery Vent Gas Flammability in Air without Inert Gas

16 tests were conducted to determine that the LFL of Li-Ion pBVG and air mixtures is 7.88±0.41 %vol Li-Ion pBVG (Figure 6.1). 13 tests were conducted to determine that the UFL of Li-Ion pBVG and air mixtures is 37.14±0.42 %vol Li-Ion pBVG (Figure 6.2).



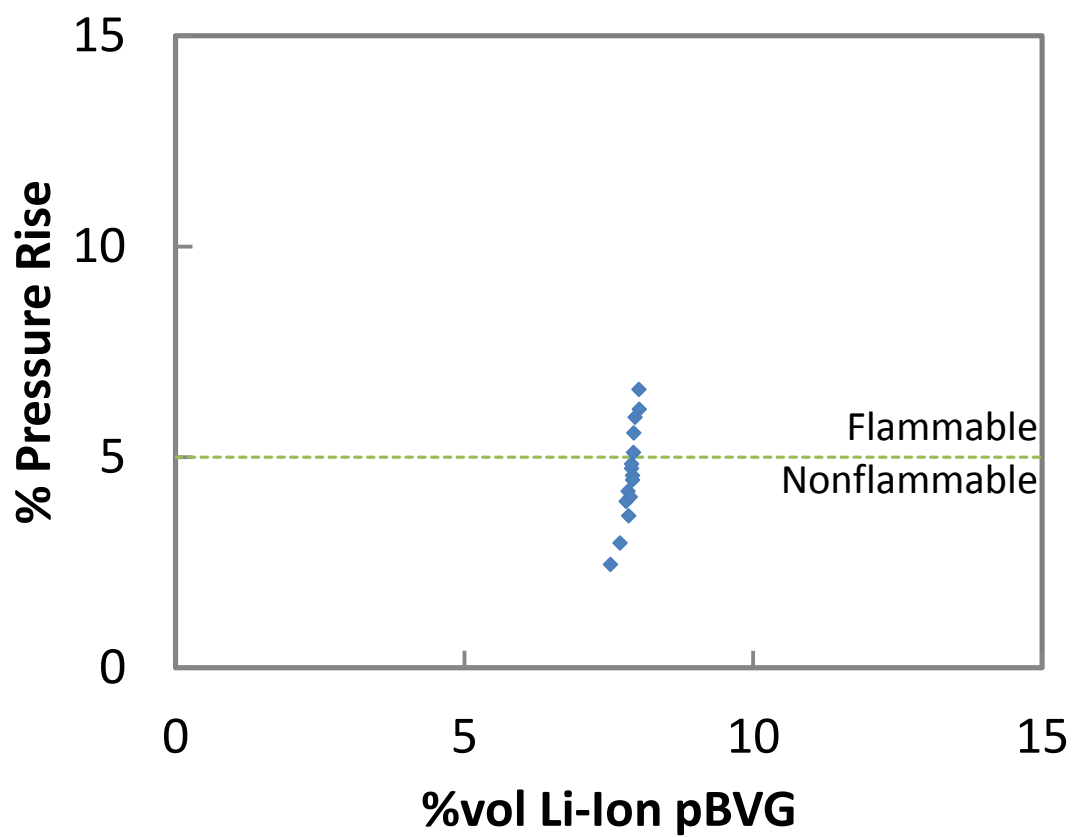


Figure 6.1: LFL of lithium-ion premixed battery vent gas in air

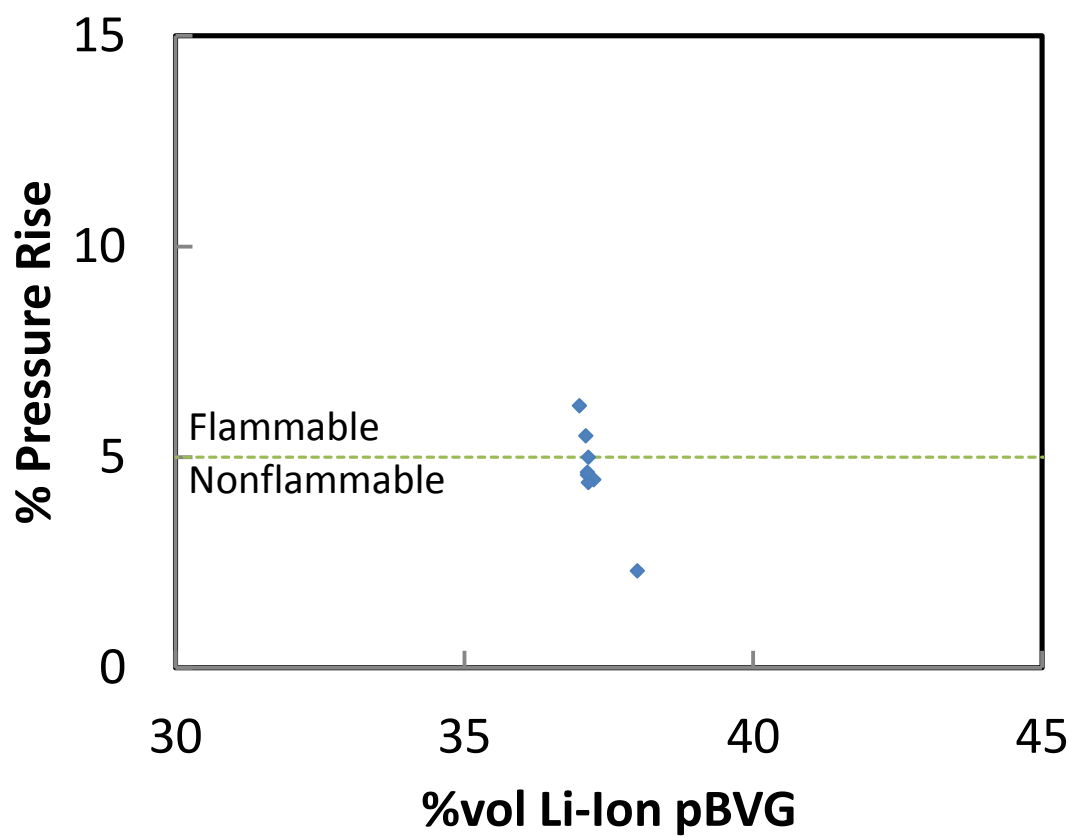


Figure 6.2: UFL of lithium-ion premixed battery vent gas in air

### **6.2.2 Lithium-Ion Premixed Battery Vent Gas Flammability in Air with 5 % Halon 1301 by Volume Addition**

17 tests were conducted to determine that the LFL Li-Ion pBVG, air, and 5 %vol Halon 1301 mixtures is  $13.80 \pm 0.49$  %vol Li-Ion pBVG (Figure 6.3). 12 tests were conducted to determine that the UFL of Li-Ion pBVG, air, and 5 %vol Halon 1301 mixtures is  $26.07 \pm 0.43$  %vol Li-Ion pBVG (Figure 6.4).

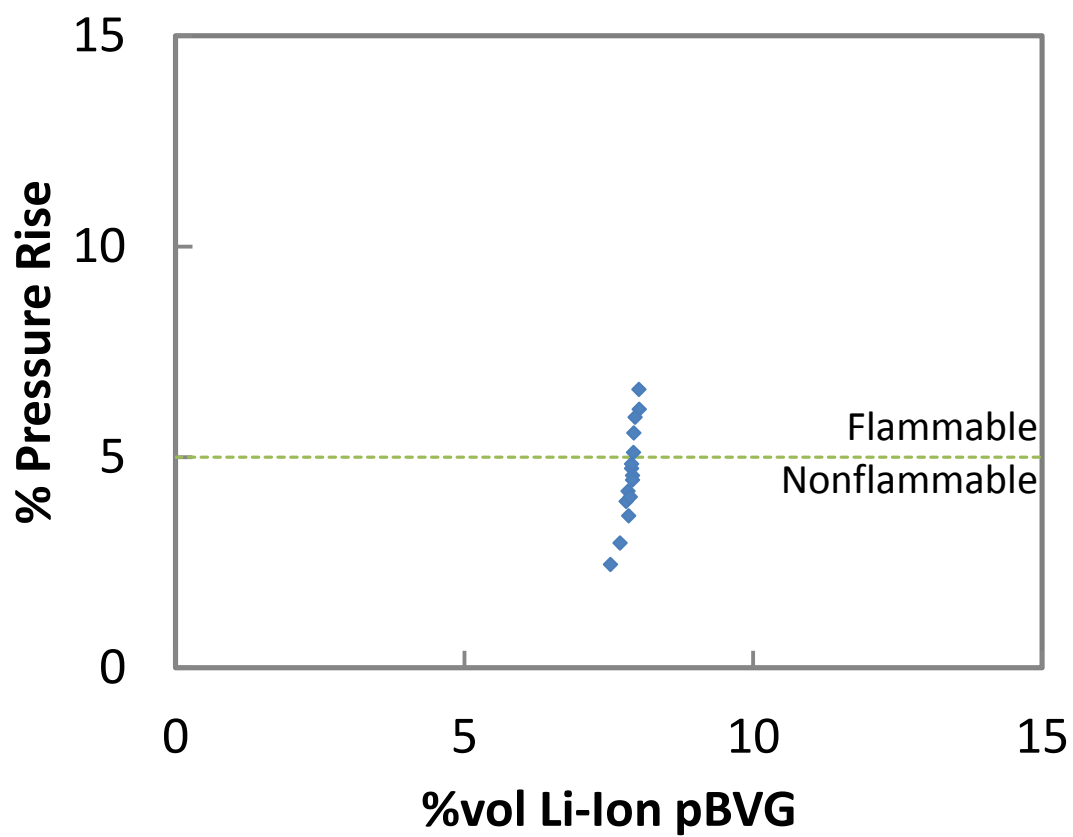


Figure 6.3: LFL of lithium-ion premixed battery vent gas in air with 5 % Halon 1301 by volume

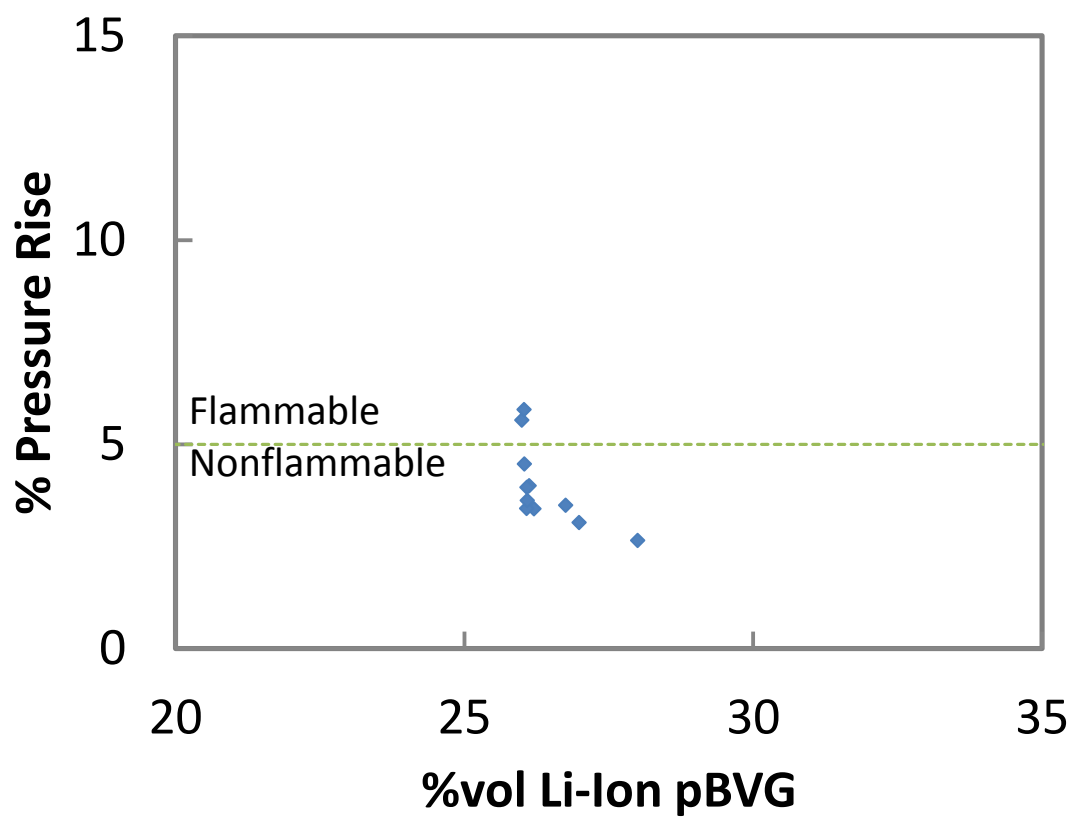


Figure 6.4: UFL of lithium-ion premixed battery vent gas in air with 5 % Halon 1301 by volume

### **6.2.3 Lithium-Ion Premixed Battery Vent Gas Flammability in Air with 7 % Halon 1301 by Volume Addition**

10 tests were conducted to determine that the LFL of Li-Ion pBVG, air, and 7 %vol Halon 1301 mixtures is  $16.15 \pm 0.40$  %vol Li-Ion pBVG (Figure 6.5). 14 tests were conducted to determine that the UFL of Li-Ion pBVG, air, and 7 %vol Halon 1301 mixtures is  $23.31 \pm 0.44$  %vol Li-Ion pBVG (Figure 6.6).

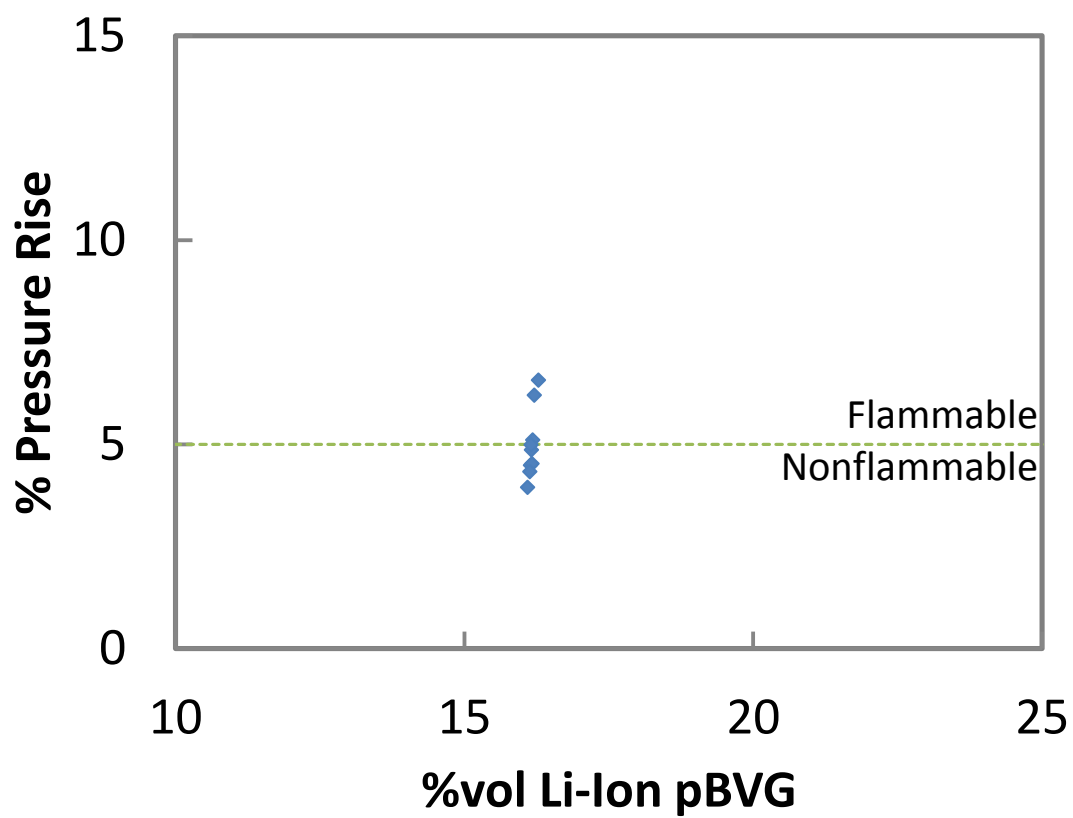


Figure 6.5: LFL of lithium-ion premixed battery vent gas in air with 7 % Halon 1301 by volume

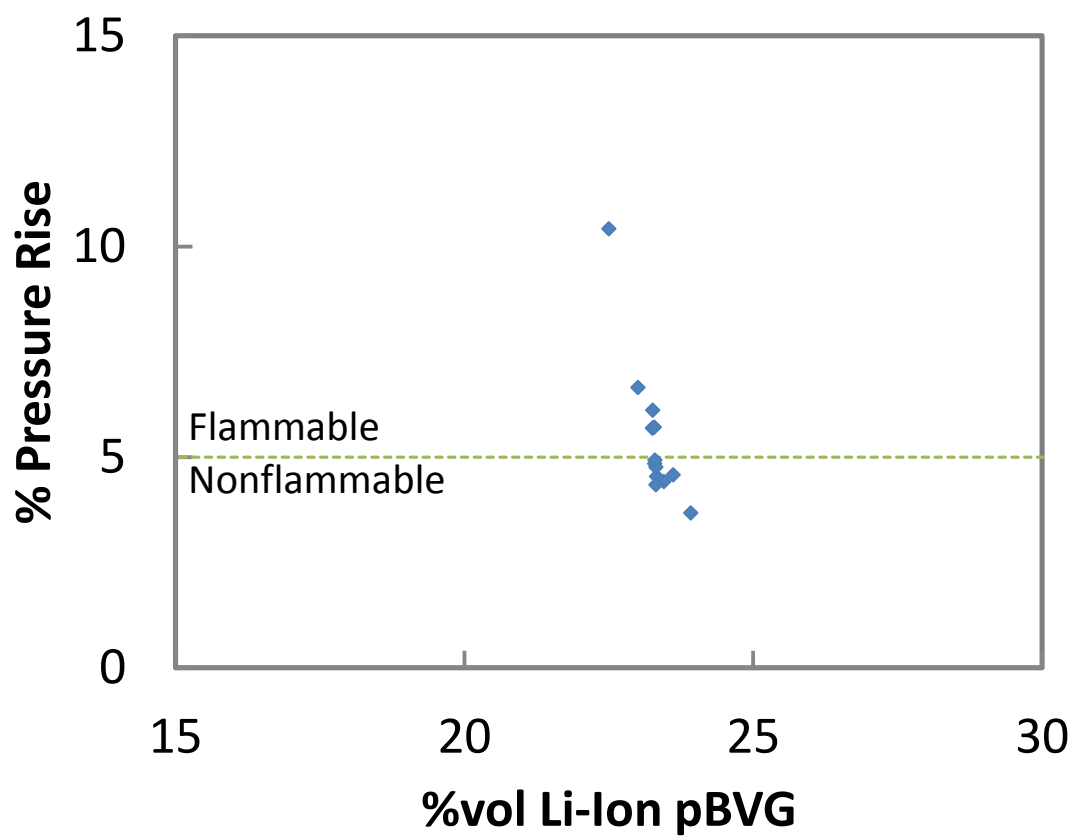


Figure 6.6: UFL of lithium-ion premixed battery vent gas in air with 7 % Halon 1301 by volume



#### **6.2.4 Lithium-Ion Premixed Battery Vent Gas Flammability in Air with 8 % Halon 1301 by Volume Addition**

8 tests were conducted to determine that the LFL of Li-Ion pBVG, air, and 8 %vol Halon 1301 mixtures is  $17.62 \pm 0.52$  %vol Li-Ion pBVG (Figure 6.7). 7 tests were conducted to determine that the UFL of Li-Ion pBVG, air, and 8 %vol Halon 1301 mixtures is  $21.84 \pm 0.65$  %vol Li-Ion pBVG (Figure 6.8).

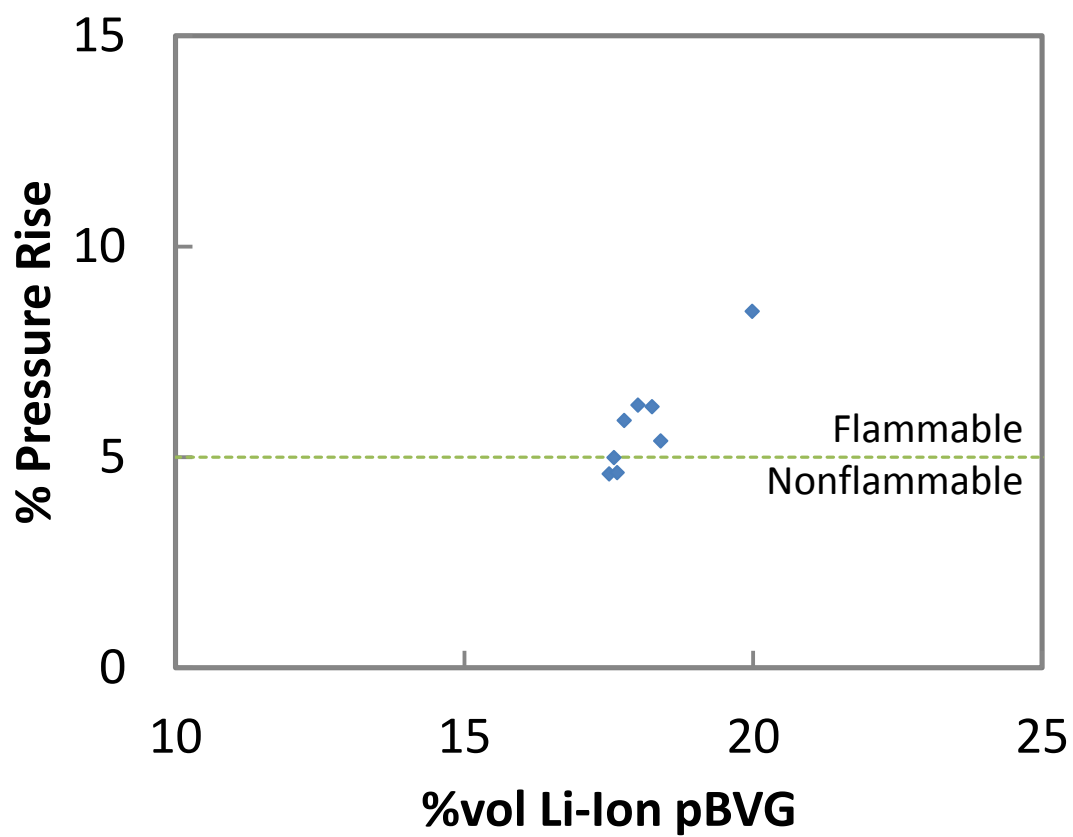


Figure 6.7: LFL of lithium-ion premixed battery vent gas in air with 8 % Halon 1301 by volume

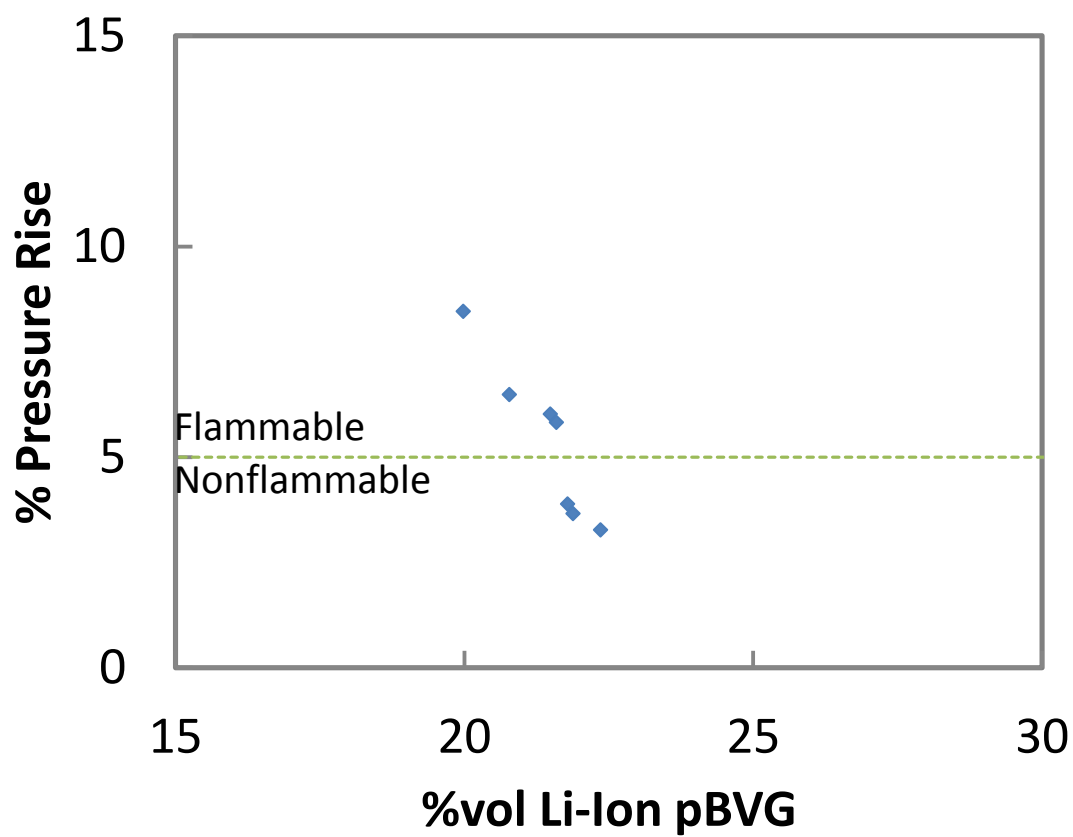


Figure 6.8: UFL of lithium-ion premixed battery vent gas in air with 8 % Halon 1301 by volume

### **6.2.5 Halon 1301 Minimum Inerting Concentration of Lithium-Ion Premixed Battery Vent Gas in Air**

34 tests were conducted to determine the minimum inerting concentration of Halon 1301 in Li-Ion pBVG and air mixtures to be  $8.59 \pm 0.52$  %vol Halon 1301 at 19.52 %vol Li-Ion pBVG (Figure 6.9).

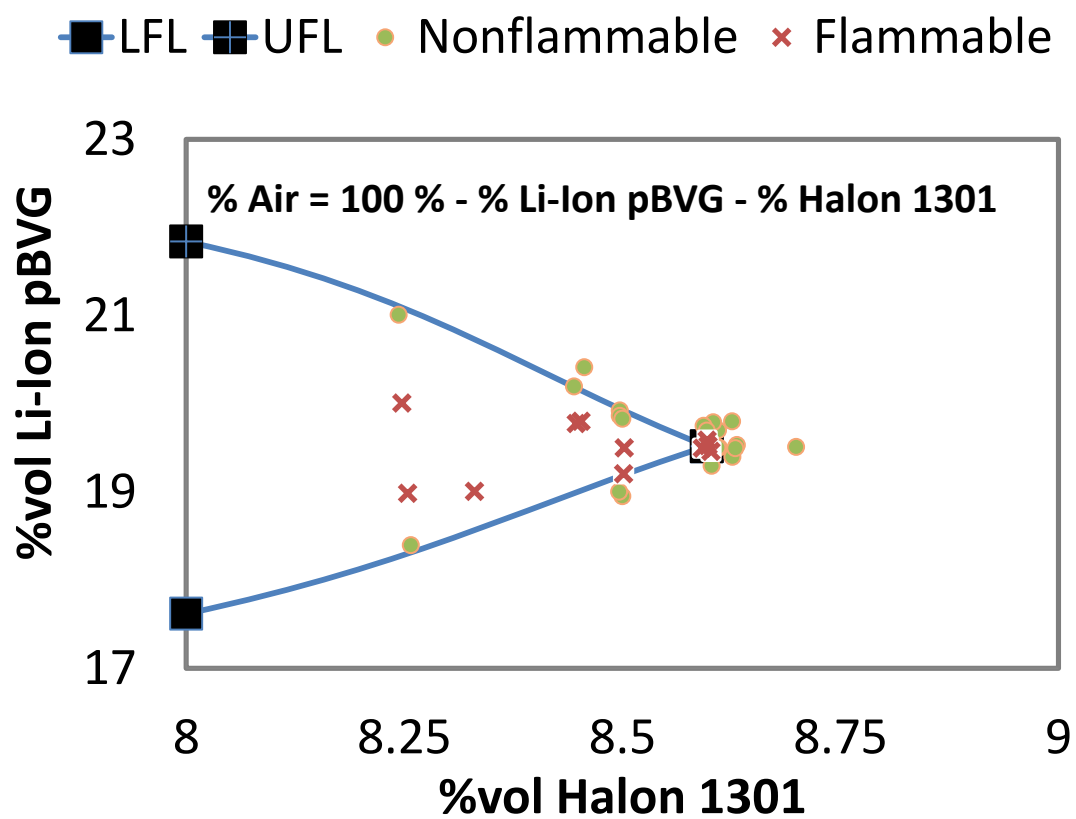


Figure 6.9: Flammability nose cap of lithium-ion premixed battery vent gas, air, and Halon 1301 mixtures

### 6.3 Summary

The 5 %vol Halon 1301 knockdown concentration and the sustained 3 %vol Halon 1301 in a Class C cargo compartment may not be sufficient in inerting Li-Ion BVG and air mixtures. At 5 %vol Halon 1301, the flammability limits range from  $13.80 \pm 0.49$  %vol to  $26.07 \pm 0.43$  %vol Li-Ion pBVG (Table 6.1). Testing suggests that  $8.59 \pm 0.52$  %vol Halon 1301 is required to yield all ratios of the Li-Ion pBVG in air inert (Table 6.2).

16 tests were conducted to determine that the LFL of Li-Ion pBVG in air mixtures to be  $7.88 \pm 0.41$  %vol Li-Ion pBVG (Figure 6.1). 13 tests were conducted to determine that the UFL of Li-Ion pBVG in air mixtures to be  $37.14 \pm 0.42$  %vol Li-Ion pBVG (Figure 6.2).

17 tests were conducted to determine that the LFL of Li-Ion pBVG air and 5 % vol Halon 1301 mixtures is  $13.80 \pm 0.49$  %vol Li-Ion pBVG (Figure 6.3). 12 tests were conducted to determine that the UFL of Li-Ion pBVG, air, and 5 %vol Halon 1301 mixtures is  $26.07 \pm 0.43$  %vol Li-Ion pBVG (Figure 6.4).

10 tests were conducted to determine that the LFL of Li-Ion pBVG, air, and 7 %vol Halon 1301 mixtures is  $16.15 \pm 0.40$  %vol Li-Ion pBVG (Figure 6.5). 14 tests were conducted to determine that the UFL of Li-Ion pBVG, air, and 7 %vol Halon 1301 mixtures is  $23.31 \pm 0.44$  %vol Li-Ion pBVG (Figure 6.6).

8 tests were conducted to determine that the LFL of Li-Ion pBVG, air, and 8 %vol Halon 1301 mixtures is  $17.62 \pm 0.52$  %vol Li-Ion pBVG (Figure 6.7). 7 tests were conducted to determine that the UFL of Li-Ion pBVG, air, and 8 %vol Halon 1301 mixtures is  $21.84 \pm 0.65$  %vol Li-Ion pBVG (Figure 6.8).

34 tests were conducted to determine the minimum inerting concentration of Halon 1301 in Li-Ion pBVG and air mixtures to be  $8.59 \pm 0.52$  %vol Halon 1301 at 19.52 %vol Li-Ion pBVG (Figure 6.9).

All of the test results are graphed together to form the flammability curve of Li-Ion pBVG, air, and Halon 1301 mixtures (Figure 6.10). The UFL constricts slightly faster than the LFL as the %vol of Halon 1301 increases. Inside the curve is considered flammable while outside is considered nonflammable. Using the graph, any ratio of Li-Ion pBVG, air, and Halon 1301 can be determined to be a flammable or nonflammable mixture.

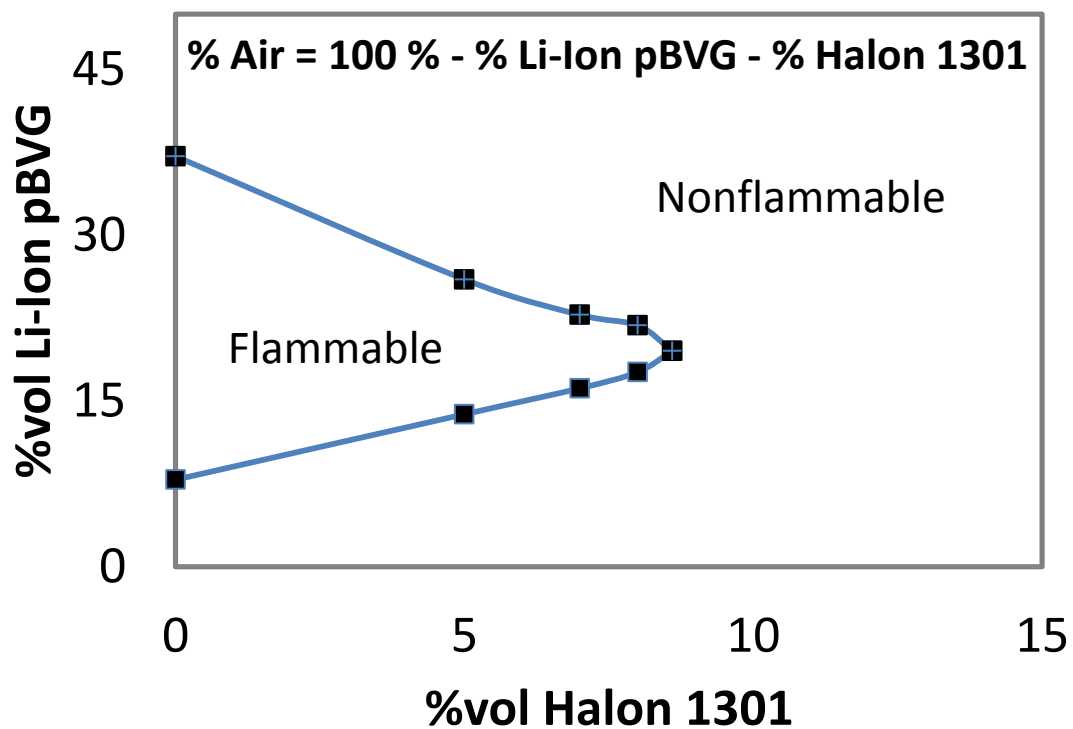


Figure 6.10: Flammability curve of lithium-ion premixed battery vent gas, air, and Halon 1301 mixtures



## Chapter VII

### Le Chatelier's Law and Fuel Mixture Flammability

#### 7.1 Introduction

Le Chatelier's mixing rule has been tested accurate for calculating the flammability limits of mixtures containing hydrogen, carbon monoxide, methane, and simpler paraffin hydrocarbons [7]. However, great inaccuracies of calculated flammability limits can be found in mixtures containing vapors such as ether or acetone [7]. Therefore, the mixing rule should not be used indiscriminately [7].

The method of calculating the flammability limits of mixed gases is outlined as follows [7]:

1. Calculate the constituents of the mixed gas neglecting the presence of air.
2. Create binary gases by combining part of or all of a nonflammable gas with one or more flammable gas and recalculate gas constituents.
3. Record the flammability limits of the mixtures' constituents from tables or curves.
4. Calculate the flammability limits of the mixture using Le Chatelier's mixing rule equation

$$L = \frac{100}{\frac{p_1}{N_1} + \frac{p_2}{N_2} + \frac{p_3}{N_3} + \dots}$$

Formula 7.1.1

Where  $L$  is either the LFL or the UFL of the gas mixture,  $p_1, p_2, p_3, \dots$  are the percentages of the mixtures constituents, and  $N_1, N_2, N_3, \dots$  are either the LFL or UFL of the individual constituents, respectively [7]. Note that if the constituents do not add up to 100 percent, one could substitute the actual total percentage.

## 7.2 Example

1. The constituents of the Li-Ion pBVG mixture used for experimental testing along with their flammability limits are shown below (Table 7.1). All of the LFLs and the UFLs are gathered from the Bureau of Mines Bulletin 503, asides from hydrogen, which was determined experimentally as described in section 5.2.1 [7].

Gas	%vol	LFL	UFL
Hydrogen	27.60	4.95	76.52
Carbon Monoxide	22.90	12.50	74.00
Carbon Dioxide	30.10	-	-
Methane	6.37	5.30	14.00
Propylene	4.48	2.40	10.30
Ethylene	2.21	3.10	32.00
Butane	1.57	1.90	8.50
Ethane	1.17	3.00	12.50
1-Butane	0.56	1.60	9.30
Propane	0.27	2.10	9.50

Table 7.1: Constituents of lithium-ion premixed battery vent gas mixture and individual flammability limits

2. The flammability limits at the ratio 1.31:1 of carbon dioxide to carbon monoxide are found using a flammability curve in Bureau of Mines Bulletin 503 [7]. Then the gas constituents' percentages are recalculated (Table 7.2).

Gas	%vol	LFL	UFL
Hydrogen	27.60	4.95	76.52
Methane	6.37	5.30	14.00
Propylene	4.48	2.40	10.30
Ethylene	2.21	3.10	32.00
Butane	1.57	1.90	8.50
Ethane	1.17	3.00	12.50
1-Butane	0.56	1.60	9.30
Propane	0.27	2.10	9.50
Carbon Dioxide to Carbon Monoxide Ratio 1.31:1	53.00	35.00	65.00

Table 7.2: Recalculated constituents of the lithium-ion premixed battery vent gas mixture for Le Chatelier's mixing rule

3. For convenience, the flammability limits are annotated above (Table 7.1 and Table 7.2).
4. Using a modified form of formula 7.1.1 to account for the constituents' percentages adding up to 99.23 %, the LFL and UFL of the mixed gas can be calculated as follows:

$$LFL = \frac{99.23}{\frac{27.6}{4.95} + \frac{6.37}{5.3} + \frac{4.48}{2.4} + \frac{2.21}{3.1} + \frac{1.57}{1.9} + \frac{1.17}{3} + \frac{0.56}{1.6} + \frac{0.27}{2.1} + \frac{53}{35}} = 7.74$$

Example 7.2.1

$$UFL = \frac{99.23}{\frac{27.6}{76.52} + \frac{6.37}{14} + \frac{4.48}{10.3} + \frac{2.21}{32} + \frac{1.57}{8.5} + \frac{1.17}{12.5} + \frac{0.56}{9.3} + \frac{0.27}{9.5} + \frac{53}{65}} = 38.86$$

Example 7.2.2

### 7.3 Discussion

The LFL and UFL of a Li-Ion pBVG at 100 % SOC can be accurately calculated using Le Chatelier's mixing rule. The LFL is calculated to be 7.74 %vol Li-Ion pBVG while the experimental is found to be 7.88 %vol Li-Ion pBVG, yielding a 1.79 % difference. The UFL is calculated to be 38.86 %vol Li-Ion pBVG while the experimental is found to be 37.14 %vol Li-Ion pBVG, yielding a 4.53 % difference.

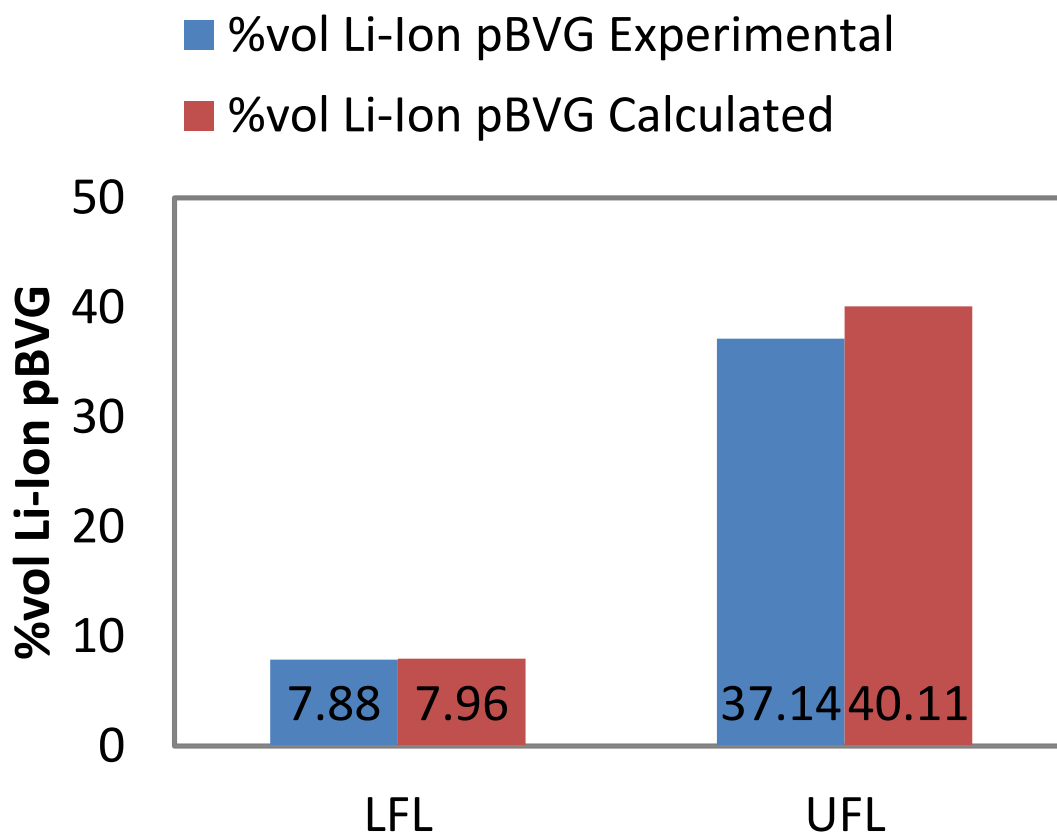


Figure 7.1: Comparison of experimental flammability limits and calculated flammability limits using Le Chatelier's mixing rule

#### **7.4 Flammability Limits Prediction by State of Charge**

Because Le Chatelier's mixing rule has been shown effective for the constituents used for testing, it is assumed that the mixing rule is effective for other states of charge. The vent gas constituents used to calculate the LFL and UFL for a 7.7 Wh lithium-ion pouch cell at 50 % SOC, 100 % SOC, and 150 % SOC are outlined in table 7.3 [19]. Le Chatelier's mixing rule is applied as outlined in section 7.3. The LFLs and UFLs used for the calculations were gathered from the Bureau of Mines Bulletin 503 [7].

Though there is no clear indication of how the SOC affects the flammability limits, the affect appears to be parabolic, with the widest flammability limits occurring around 100 % SOC and decreasing flammability limits as the SOC either decreases or increases (Table 7.4 and Figure 7.3). However, more testing at other states of charge are required to confirm this observation.

<b>Gas</b>	<b>50 % SOC</b>	<b>100 % SOC</b>	<b>150 % SOC</b>
Hydrogen	30	27.7	29.7
Carbon Monoxide	3.61	22.9	24.5
Carbon Dioxide	32.3	30	20.9
Methane	5.78	6.39	8.21
Propylene	8.16	4.52	0.013
Ethylene	5.57	2.19	10.8
1-Butane	0.67	0.56	0.39
Ethane	2.75	1.16	1.32
Butane	2.55	1.58	0.60
propane	0.68	0.26	2.54
Hexanes	4.94	2.32	8.21
Benzene	0.14	0.11	0.33
Toluene	0.061	0.018	0.052
Isopentane	0.45	0.07	0.036
n-Pentane	19.4	0.73	0.3
Ethyl-Benzene	0.009	0.002	0.003
Isobutane	0.41	0.2	0.13

Table 7.3: Vent gas constituents for a single 7.7 Wh lithium-ion pouch cell at various states of charge [19]

<b>SOC</b>	<b>LFL</b>	<b>UFL</b>	<b>Flammability Range</b>
50 % SOC	4.6	25.1	20.5
100 % SOC	6.8	34.0	27.2
150 % SOC	4.8	29.3	24.4

Table 7.4: Flammability limits for vent gas of a single 7.7 Wh lithium-ion pouch cell at various states of charge

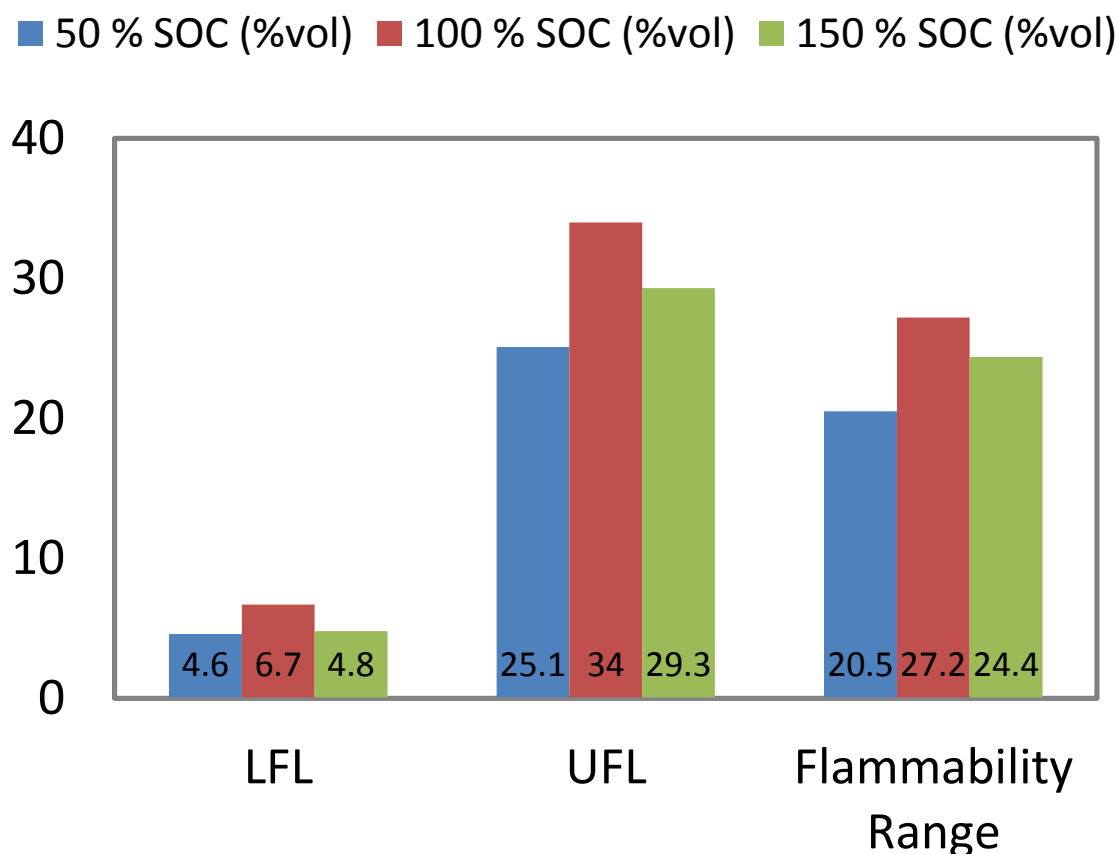


Figure 7.2: Predicted flammability Limits for vent gas of a single 7.7 Wh lithium-ion pouch cell at various states of charge

## 7.5 Summary

Le Chatelier's mixing rule has been shown to be an effective measure for estimating the flammability limits of Li-Ion pBVes. The calculated and experimentally determined LFL and UFL have a 1.79 % and a 4.53 % difference, respectively (Figure 7.1). Both are within a reasonable range of uncertainty. The SOC affects the flammability limits in an apparent parabolic manner, where the widest flammability limits are at or near 100 % SOC (Figure 7.2).

## Chapter VIII

### Conclusions and Future Work

#### 8.1 Summary and Conclusions

The 5 %vol Halon 1301 knockdown concentration and the sustained 3 %vol Halon 1301 in a Class C cargo compartment may not be sufficient at inerting lithium-ion battery vent gas and air mixtures [2]. At 5 %vol Halon 1301 the flammability limits range from 13.80 %vol to 26.07 %vol lithium-ion premixed battery vent gas (Li-Ion pBVG). Testing suggests that 8.59 %vol Halon 1301 is required to render all ratios of the Li-Ion pBVG in air inert.

The lower flammability limit (LFL) and upper flammability limit (UFL) of hydrogen and air mixtures are 4.95 %vol and 76.52 %vol hydrogen respectively. With the addition of 10 %vol and 20 %vol Halon 1301 the LFL is 9.02 %vol and 11.55 %vol hydrogen, respectively and the UFL is 45.70 %vol, and 28.39 %vol hydrogen, respectively. The minimum inerting concentration (MIC) of Halon 1301 in hydrogen and air mixtures is 26.72 %vol Halon 1301 at 16.2 %vol hydrogen.

The LFL and UFL of Li-Ion pBVG and air mixtures are 7.88 %vol and 37.14 %vol Li-Ion pBVG, respectively. With the addition of 5 %vol, 7 %vol, and 8 %vol Halon 1301 the LFL is 13.80 %vol, 16.15 %vol, and 17.62 % vol Li-Ion pBVG, respectively, and the UFL is 26.07 %vol, 23.31 %vol, and 21.84 %vol Li-Ion pBVG, respectively. The MIC of Halon 1301 in Li-Ion pBVG and air mixtures is 8.59 %vol Halon 1301 at 19.52 %vol Li-Ion pBVG.



Le Chatelier's mixing rule has been shown to be an effective measure for estimating the flammability limits of Li-Ion pBVes. The LFL has a 1.79 % difference while the UFL has a 4.53 % difference. Both are within a reasonable range of uncertainty. The SOC affects the flammability limits in an apparent parabolic manner, where the widest flammability limits are at or near 100 % SOC.

## **8.2 Future Work**

Knowledge of flammability limits and flammability curves are essential in analyzing and mitigating the risks associated with various gases. There is still more to study in the field of lithium battery vent gas flammability for the application of aircraft fire safety.

For example, testing can be conducted to determine the flammability limits and maximum pressure rise of lithium batteries of varying sizes or cell chemistry at varying states of charge. Testing can also be conducted to determine the effectiveness of various gases or gas mixtures in inerting lithium battery vent gases.

Flammability testing is laborious. Therefore, there are plans to automate the test apparatus. This will allow for safer, more accurate, and quicker testing while reducing labor.

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## APPENDIX

### A-1 14 CRF 25.857 Cargo Compartment Classification

Title 14 Code of Federal Regulations (CRF) Part 25 describes the legal requirements for transport aircraft within the United States. Note that Class D cargo compartments have been upgraded to Class C. CRF 25.857 is shown below [5].

(a) *Class A*; A Class A cargo or baggage compartment is one in which—

(1) The presence of a fire would be easily discovered by a crewmember while at his station; and

(2) Each part of the compartment is easily accessible in flight.

(b) *Class B*. A Class B cargo or baggage compartment is one in which—

(1) There is sufficient access in flight to enable a crewmember to effectively

reach any part of the compartment with the contents of a hand fire extinguisher;

(2) When the access provisions are being used, no hazardous quantity of smoke, flames, or extinguishing agent, will enter any compartment occupied by the crew or passengers;

(3) There is a separate approved smoke detector or fire detector system to give warning at the pilot or flight engineer station.

(c) *Class C.* A Class C cargo or baggage compartment is one not meeting the requirements for either a Class A or B compartment but in which—

- (1) There is a separate approved smoke detector or fire detector system to give warning at the pilot or flight engineer station;
- (2) There is an approved built-in fire extinguishing or suppression system controllable from the cockpit.
- (3) There are means to exclude hazardous quantities of smoke, flames, or extinguishing agent, from any compartment occupied by the crew or passengers;
- (4) There are means to control ventilation and drafts within the compartment so that the extinguishing agent used can control any fire that may start within the compartment.

(d) [Reserved]

(e) *Class E.* A Class E cargo compartment is one on airplanes used only for the carriage of cargo and in which—

- (1) [Reserved]
- (2) There is a separate approved smoke or fire detector system to give warning at the pilot or flight engineer station;
- (3) There are means to shut off the ventilating airflow to, or within, the compartment, and the controls for these means are accessible to the flight crew in the crew compartment;

- (4) There are means to exclude hazardous quantities of smoke, flames, or noxious gases, from the flight crew compartment; and
- (5) The required crew emergency exits are accessible under any cargo loading condition.

[Doc. No. 5066, 29 FR 18291, Dec. 24, 1964, as amended by Amdt. 25-32, 37 FR 3972, Feb. 24, 1972; Amdt. 25-60, 51 FR 18243, May 16, 1986; Amdt. 25-93, 63 FR 8048, Feb. 17, 1998]