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Introduction:

Energizer® lithium iron disulfide differs from alkaline batteries in chemistry and construction. They are built in a spiral construction featuring two long, thin electrodes rolled together to form a jellyroll shape. This shape provides almost 20 times more interfacial surface area than a standard alkaline. This large interface helps to meet the power demands of many of today's devices. Lithium is the lightest, most active metal. When this powerful metal is paired with iron disulfide, this energy is available at a voltage suitable for 1.5 volt applications.



AA "Ultimate" Lithium 4-Pack

Energizer® successfully produced the first commercially available "AA" size 1.5 volt lithium battery in 1989. The 1.5 volt "AAA" size followed in 2004.

Electrodes in lithium iron disulfide batteries are isolated from one another by a highly engineered microporous polymer membrane. This membrane allows ions to move easily during normal use, but restricts this movement in certain abuse situations to ensure superior product performance and safety. Lithium iron disulfide batteries contain a non-aqueous electrolyte designed to operate even in extreme temperatures from as low as -40°C up to +60°C. They also include a resettable overcurrent safety device that protects the user by switching the battery off if it is misused in devices.

Some of the advantages of the lithium iron disulfide ($LiFeS_2$) system over the alkaline chemistry are:

- Direct drop-in compatibility in applications using primary 1.5 volt "AA" and "AAA" battery sizes.
- Far greater power than other primary battery types.
- Provides longer service than other primary battery types in moderate to heavy

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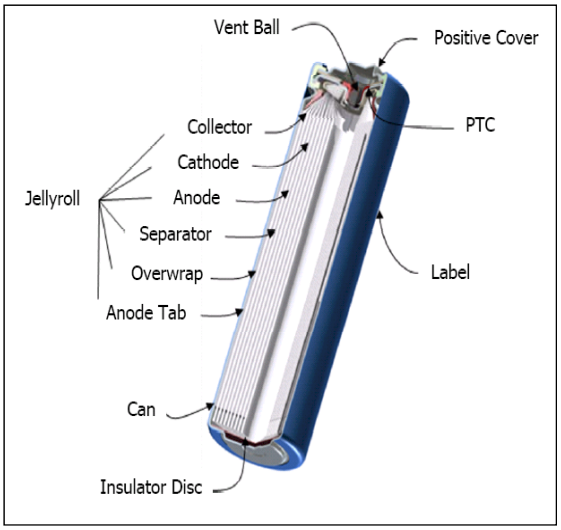
drain applications.

- Greater service advantage over other primary battery types at low temperature extremes operating at -40°C.
- Higher operating voltage and flatter discharge curve than other primary battery types.
- Superior leakage resistance compared to other primary battery types.
- Outstanding service maintenance when stored at ambient conditions.
- Considerably lighter than other battery types.
- Good service maintenance after high temperature storage up to +60°C.
- No added mercury, cadmium, or lead.

As power demands of new devices continue to increase and high drain devices become more prevalent with consumers, *Energizer*® lithium iron disulfide batteries provide the optimum performance consumers demand.

Battery Description:

Cylindrical lithium iron disulfide batteries use lithium for the anode, iron disulfide for the cathode, and a lithium salt in an organic solvent blend as the electrolyte. A cutaway (Fig. 1) of a typical cylindrical $LiFeS_2$ battery is illustrated in the following diagram:
Click here for larger view



Anode - lithium metal
Cathode – iron disulfide on an aluminum foil substrate
Separator – polyolefin
Electrolyte – lithium salt / organic solvent
Jellyroll construction – spiral wound multiple layers of anode/separator/cathode material to produce a high surface area for high power cell design
Vent ball – safety mechanism that provides internal pressure release
Positive and negative contact surfaces - nickel-plated steel
Non-conductive plastic film label - electrically insulates the battery
Positive Temperature Coefficient (PTC) – over current safety device

(Fig. 1) Typical Cylindrical Lithium Iron Disulfide Battery

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The term “lithium battery” refers to many different chemistries utilizing lithium as the anode but differing in cathode material, electrolyte, and construction. They may be classified in several ways, but one convenient method is by the cathode material and voltage. Using an iron disulfide cathode gives a battery with a nominal voltage of 1.5 volts. Most other lithium batteries are 3.0 volt systems using cathodes comprising either solids (manganese dioxide or carbon monofluoride) or highly toxic liquids (sulfur dioxide or thionyl chloride). Finally, lithium batteries should not be confused with lithium ion rechargeable batteries. Lithium ion batteries do not contain metallic lithium.

Under rating current drain rates (~200mA), typical of many commercial devices, the “AA” size $LiFeS_2$ battery has a specific energy density of ~297 Wh/kg compared to a comparable size alkaline of ~143 Wh/kg.

The characteristics that make lithium an exceptional electrode material for high energy density batteries include, low electrode potential and very high conductivity. It is soft and malleable and can be extruded into thin foils. Lithium reacts with water and for this reason must be used with a non-aqueous electrolyte.

The choice of cathode materials is critical when considering voltage, high energy density, high rate performance, and electrolyte compatibility. Other considerations include low cost, environmentally friendly, and stability. The choice of FeS_2 as a cathode material is unique because the chemical reaction with lithium results in an open circuit voltage (OCV) of 1.8 volts. Other cathode materials combined with lithium will produce battery voltages above 2.0 volts.

Although the higher OCV of the $LiFeS_2$ system is 1.8 volts, the nominal or rated voltage is 1.5 volts which makes it a suitable replacement for alkaline and nickel systems. The battery voltage will drop when it is placed under load. For this reason, the higher OCV will typically not damage electronic components, but device designers should take into consideration that the OCV of fresh batteries can range from 1.79 to 1.83V. $LiFeS_2$ batteries fully meet the ANSI specification for a 1.5V battery. When a drain has been applied to the battery, the OCV drops dramatically and then slowly recovers with time. The OCV for a battery can be misleading. A “good” battery will generally have an OCV >1.74 volts. Any battery with an OCV <1.70 (after it has been allowed to recover) is completely discharged. Although an alkaline battery may read “good” at 1.6 volts, this reading on a $LiFeS_2$ battery indicates the product has been discharged. The jellyroll battery design gives the battery excellent high rate performance. The non-aqueous electrolyte used in $LiFeS_2$ battery provides excellent low temperature performance.

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Under high temperature operating or storage, it is not uncommon to experience some electrolyte odor. This odor is due to transmission of ethers (i.e. 1, 2-dimethoxyethane and 1, 3-dioxolane) through the seal. The odor threshold for these organics is on the order of a few parts per million, which does not indicate leakage. The ethers can have a noticeable odor, but the actual amount of vapors present is very low. Potential exposure is well below the American Conference of Governmental Industrial Hygienists (ACGIH) time weighted average limit and other industry standards.

The overall discharge reaction of the $LiFeS_2$ construction takes place in two steps. The first step: $2Li+FeS_2 \rightarrow Li_2FeS_2$. The second step follows: $2Li+Li_2FeS_2 \rightarrow Fe+2Li_2S$. Typically the two step discharge can be seen at low drain rates of approximately ten milliamps or less and during higher drains at elevated temperatures.

The discharge characteristics of batteries can vary depending upon whether they are discharged at a constant resistance, constant current, or constant power drain. Due to the unique characteristics of the lithium chemical system, the battery will maintain a high average operating voltage compared to other systems throughout the life of the discharge. This is particularly important for constant power devices that can better take advantage of the higher voltage. As the battery voltage decreases, the current drain increases to maintain constant power to the device. Therefore, the higher voltage of lithium iron disulfide lowers the current drain on the battery and longer run times.

Temperature Effects on Performance:

Lithium iron disulfide ($LiFeS_2$) batteries have a much lower sensitivity to temperature compared to other chemical systems. The recommended operating temperature range is -40°C to +60°C (-40°F to +140°F). As with all battery systems, service life is reduced as the discharge temperature is lowered below room temperature (Fig. 2).

Batteries generate power through chemical reactions and these typically run much more slowly at lower temperatures. However, even at -40°C, the $LiFeS_2$ batteries perform well at the rating drain 200 mA. $LiFeS_2$ batteries can deliver approximately full rated capacity at -40°C if they are discharged at 25 mA. Thus, at these rates, the batteries give comparable performance over the entire 100°C operating range.

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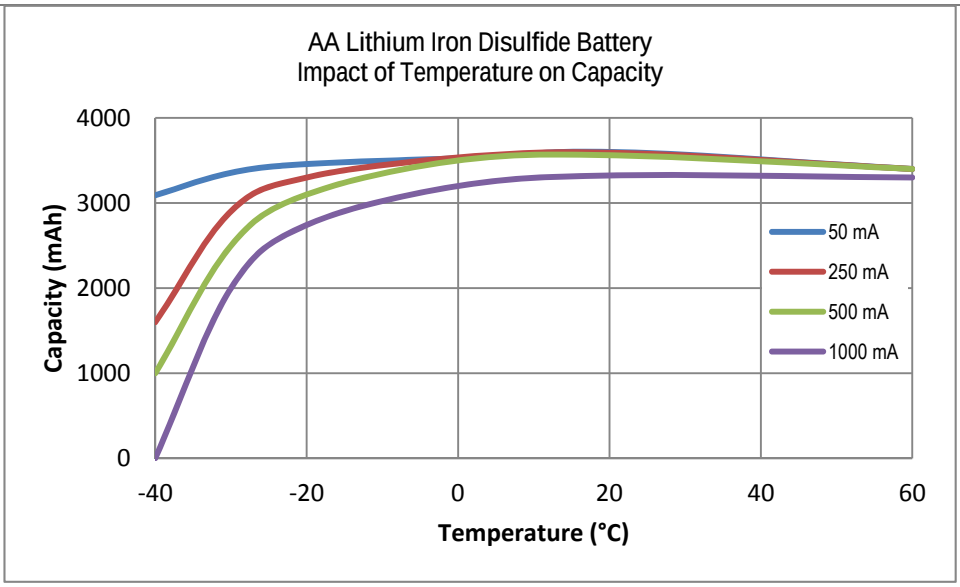
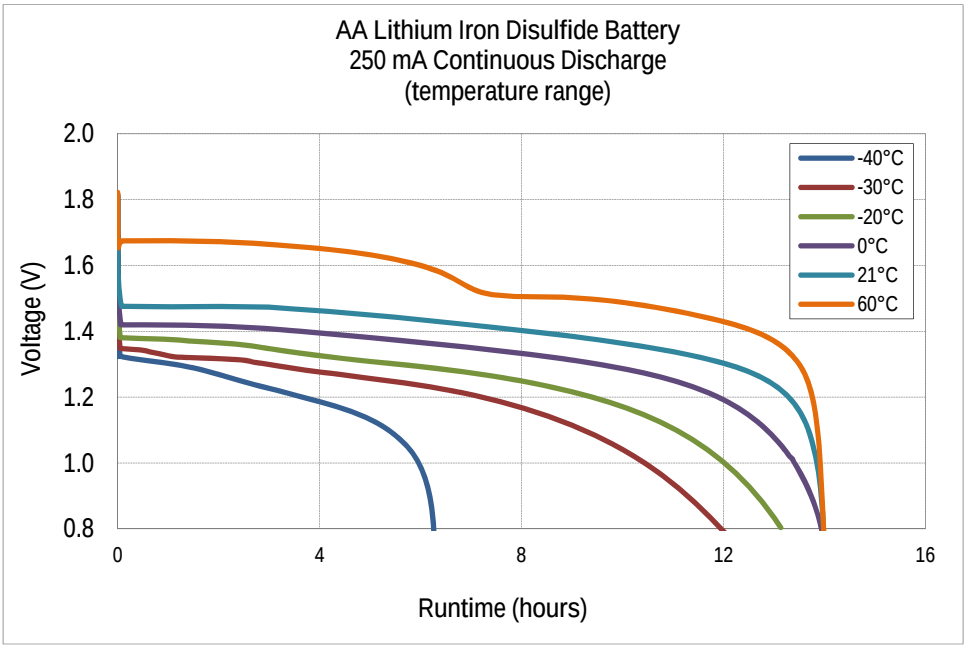


(Fig. 2) Temperature Effect on Capacity

Cold temperatures also lower the operating voltage thereby reducing the energy output (Fig 3). Battery capacity is not lost due to cold temperature use, rather it is more difficult to access the battery's full potential due to the slowing of the electrochemical reactions, reducing capacity at high drain rates.



(Fig. 3) Temperature Effect on Performance

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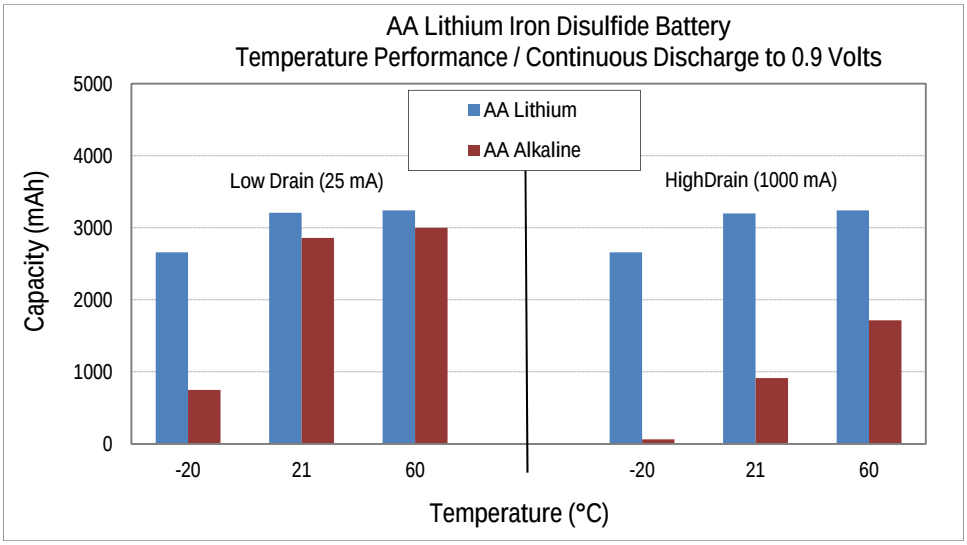
When comparing cold temperature performance of the $LiFeS_2$ battery versus an alkaline based aqueous system, the $LiFeS_2$ system is affected much less across a range of drain rates (Fig. 4) and operates at temperatures where alkaline batteries do not run at all. This is due to the use of a non-aqueous electrolyte and the high surface area jellyroll construction. In particular, *Energizer*® patented electrolyte has the unique property of actually increasing in conductivity as the temperature drops, in contrast to electrolytes used in other lithium batteries.



(Fig. 4) Temperature Effect on Performance versus Alkaline

Conversely, warm temperatures can boost battery performance in very high drain continuous applications that increase the battery temperature (Fig.5).

In some applications there may be further limits on the maximum discharge temperature due to current limiting safety features of the battery. The $LiFeS_2$ battery utilizes a PTC (positive temperature coefficient over current safety device) that is designed to reversibly shut down the battery at high temperatures.

Both ambient temperature and the internal battery heating that occurs during discharge will affect the operation of the PTC.

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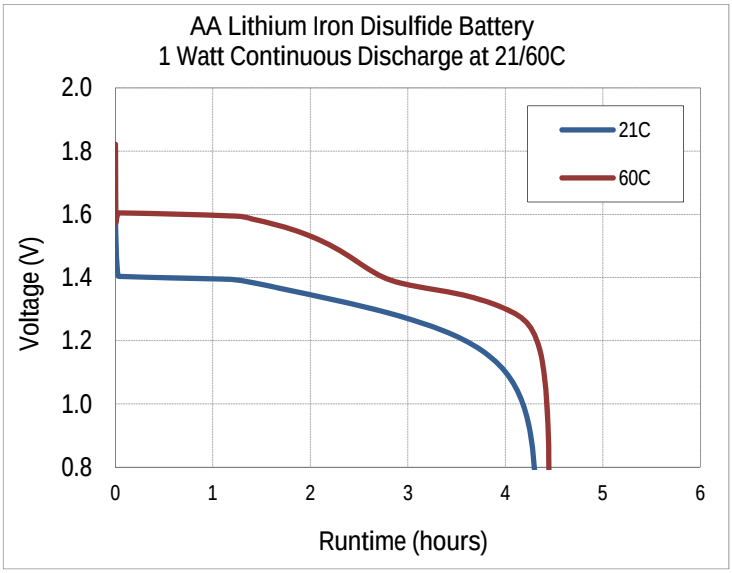
The higher the rate of discharge (a heavy drain or load on the battery), the more heat is generated that could cause the PTC to activate. In low to moderate drain applications, less than 500 mA, the heat dissipates and should not activate the PTC. However, a high ambient temperature combined with a high drain application increases the likelihood of PTC activation. Moreover, many applications use power intermittently and this can greatly mitigate any temperature rise and prevent PTC activation. While PTC activation in these rare scenarios may be a nuisance, the PTC is critical to battery safety.



(Fig. 5) Elevated Temperature Effect on Performance

The batteries and device should once again perform normally once the battery has time to cool down.

Device manufacturers must consider all of the following that can affect internal heating of $LiFeS_2$ batteries during discharge.

- Surrounding air temperature
- Thermal insulating properties of the battery container
- Heat generated by equipment components
- Cumulative heating effects of multiple batteries
- Discharge rate(s) and duration(s)
- Frequency and length of rest periods

Comparison to other Chemical Systems:

Lithium iron disulfide batteries have a higher operating voltage than alkaline and rechargeable nickel metal hydride (NiMH) batteries and flatter discharge profile versus alkaline. These characteristics result in higher energy density (Wh/L) and specific

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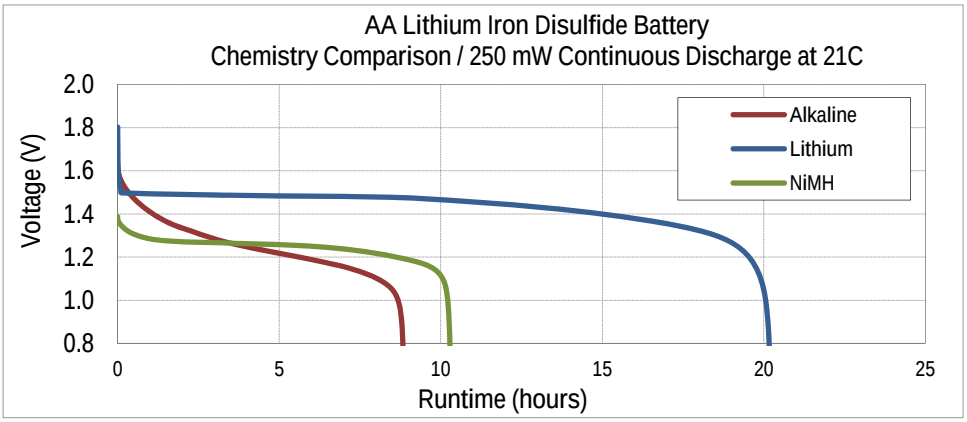
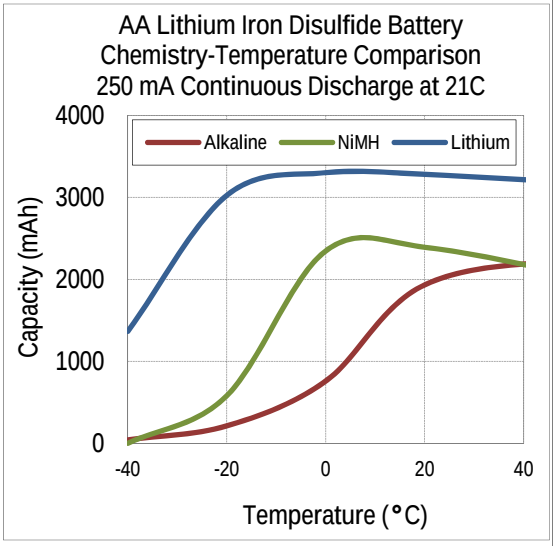
energy (Wh/kg), especially in heavier drain applications where the operating voltage differences are the greatest.

The flatter discharge curve allows for consistent performance throughout the life of the battery. The performance advantages of lithium over alkaline increases dramatically as drain rates increase due to the jellyroll construction and better high rate efficiency.
The following chart (Fig. 6) shows the relative constant power performance of an AA size battery for the lithium, alkaline and NiMH chemistries.



(Fig. 6) Relative Constant Power Performance of an AA Size Battery (different chemistries)

Lithium iron disulfide batteries are suitable for use across a broad temperature range. While at elevated temperatures, all chemistries show minimal change in performance versus ambient. At low temperatures, the lithium battery offers more performance than alkaline or NiMH chemistries. The following graph (Fig. 7) shows the impact of temperature on AA size lithium, alkaline and NiMH under a 250 mA drain rate to a 0.9 volt cutoff.



(Fig. 7) Impact of Temperature on AA Size Lithium, Alkaline and

Additional performance comparisons can be found on the individual datasheets listed on the Technical Information Website. Additional $LiFeS_2$ advantages are listed in the following table:

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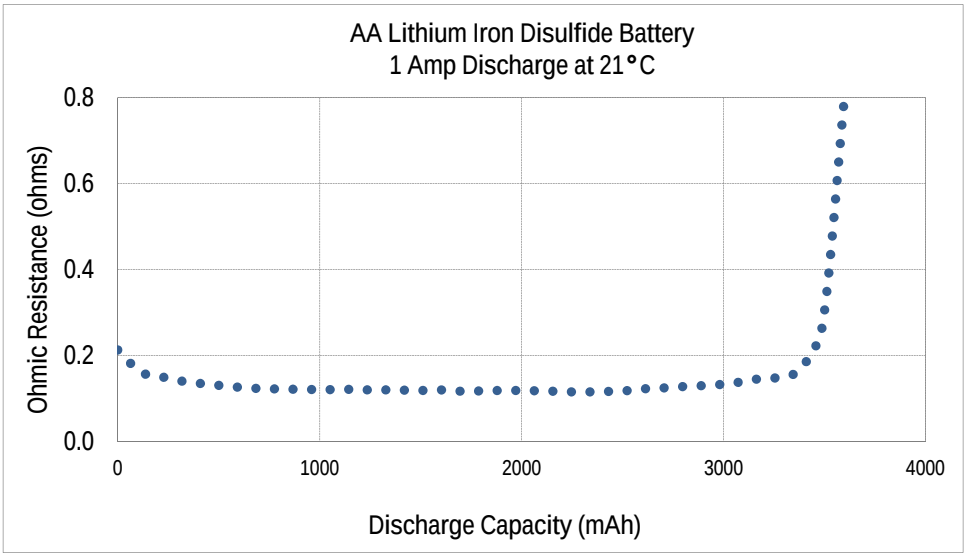
Characteristics	Lithium	Alkaline	NiMH
Cold Temp Performance	Superior	Good	Superior
Weight	33% < Alkaline	33% > Lithium	33% > Alkaline
Shelf Life	20+ Years	5 to 10 Years	3 to 5 Years
Leakage Resistance	Superior	Good	Good
Discharge Curve	Flat	Sloping	Flat
High Rate Capability	Superior	Good	Superior

Internal Resistance:

Another method used to estimate true IR uses a current interrupt technique (CIT), whereby the rapid change in battery voltage during discharge is periodically and briefly interrupted to estimate the battery IR. This has the advantage of measuring the battery IR under realistic drain rates and also enables one to measure the change in battery IR during discharge. The following graph (Fig. 9) shows that there is very little change in battery IR during discharge and in fact it actually improves slightly.



(Fig. 9) True IR of a typical AA size lithium iron disulfide battery during a 1 amp discharge.

True IR is not adversely affected by temperature (almost no change between -20 and 40°C), discharge current, depth of discharge, battery age or storage at elevated temperatures.

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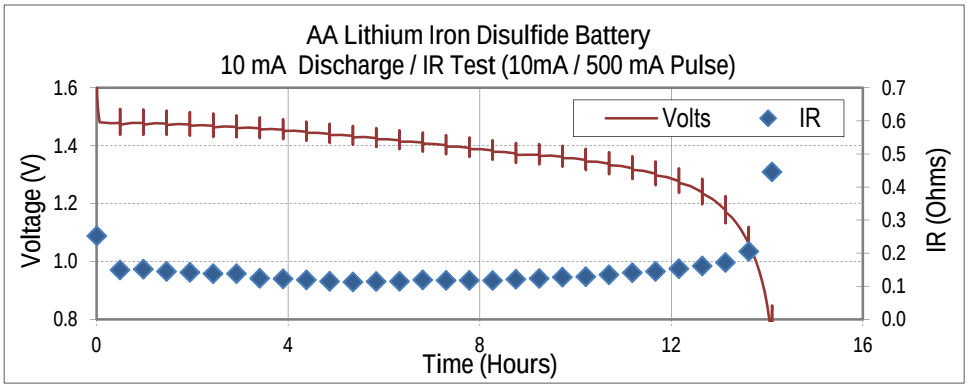
The resistance to current flow that a battery exhibits can depend on the current drain being applied and especially on the time scale of the measurement. The methods described above measure battery IR over a very short time scale. In actual device applications, various polarization effects occurring over longer times will reduce the battery's operating voltage and appear as resistance contributors. From a design engineers' point of view, a more important metric of the battery's performance may be the *effective* IR which is the impedance during actual usage.

Typically, effective IR is greater than the true IR. However, since the effective IR depends on the load and timescale, any measurement that relies upon the OCV of the battery prior to a test should not be used. A commonly used method whereby the resistance is calculated as shown below must not be used with AA size lithium iron disulfide batteries as the values are much higher than the real values. This is due to the initial OCV of AA size lithium iron disulfide batteries being higher than the OCV of the chemistry that actually controls the battery's discharge performance.

Effective IR = (OCV - CCV) / Current Applied (not valid for lithium iron disulfide batteries) Effective IR can be calculated by using a double current pulse CCV measurement whereby the system first applies a low current drain pulse to reduce the OCV and then applies a heavier pulse. The effective IR at the higher drain rate can then be calculated by the voltage difference between the two pulses. The timing of the pulses should reflect the timescale of interest to the application. For example, apply a 10 mA pulse for 50 ms followed by a 500 mA pulse for 100 ms (Fig. 10). Values of effective battery IR measured using this regime are about 100 mΩ.



(Fig. 10) IR of a typical AA size lithium iron disulfide battery during discharge.

Effective IR = $(CCV_1 - CCV_2) / (Current_2 - Current_1)$

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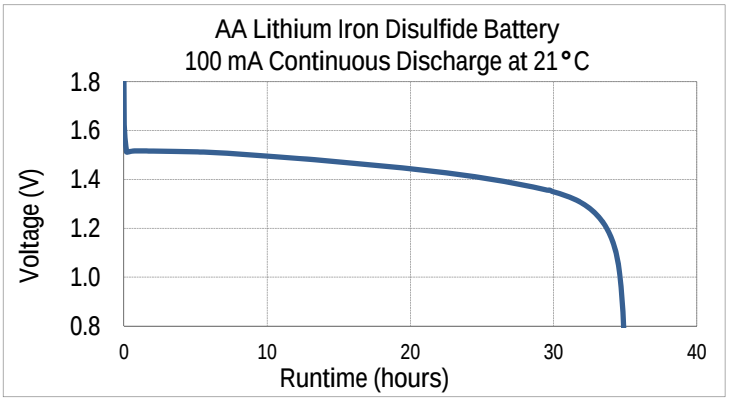
Again, caution must be exercised in comparing true IR values to effective IR readings or those obtained using other measurement methods. In particular, impedance measurements at 1 kHz or resistance values based on OCV-CCV differences typically overestimate the IR for lithium iron disulfide batteries. Overall, the lithium iron disulfide battery IR changes very little with age, discharge rate, depth of discharge and temperatures of -20 to 40°C. While impedance at lower frequencies can increase during aging, this has very little effect on the impedance of the battery when it is subsequently placed under load.

Capacity:

Battery capacity is typically expressed in terms of milli-Amp hours (mAh). This is an indication of how long a battery will provide service at a specific drain rate to a specific cutoff voltage. For example, the following discharge curve (Fig. 11) is for the AA size lithium iron disulfide battery being discharged at 100 mA to a 0.9 volt cutoff.



(Fig. 11) 100 mA Continuous Discharge

The available capacity can then be calculated by multiplying the drain rate (mA) by the hours to the cutoff voltage. For example, this AA battery would have a capacity of (100 mA X 36 hours) 3600 mAh at a 100 mA drain to a 0.9 volt cutoff.

The mAh capacity of lithium iron disulfide batteries will vary with the drain rate and the cutoff voltage. Due to the jellyroll construction and multiple layers of active material, the lithium iron disulfide battery is extremely efficient across multiple drains and is much less sensitive to both the drain rate and voltage cut than alkaline batteries. The flat discharge profile and high operating voltage of lithium iron disulfide allow for longer, consistent run times in high drain / high power devices as shown below (Fig. 12).

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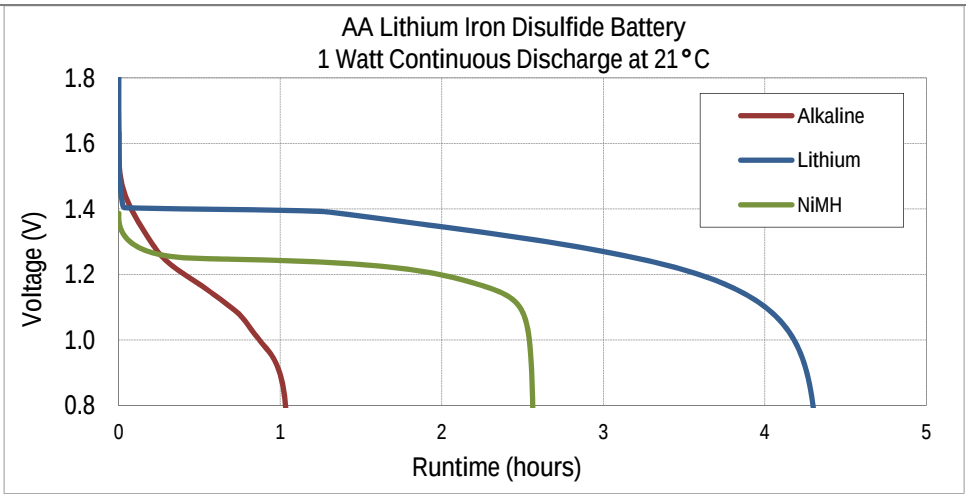

(Fig. 12) Chemistry Discharge Curve Characteristics

The application cutoff voltage will also impact the amount of service delivered by the battery. A high cutoff voltage will result in leaving more of the battery's capacity unused. To maximize usage of the available capacity, it is recommended that devices should be designed with a voltage cutoff of 0.8 volts per battery. At this point, a majority of the battery's usable capacity has been removed. However, lithium iron disulfide operates at a higher voltage and is well suited for high cutoff devices. Ideally, to avoid deep discharging batteries, one should not discharge them below 0.5 volts.

In high drain pulse applications, the duty cycle can impact battery efficiency. A very light duty cycle will typically allow the battery more time to recover and extend service compared to a continuous drain. The amount of additional service will depend on the drain rate, and the duty cycle (ON time and OFF time of the pulse). Due to $LiFeS_2$ high rate capability, the effect of intermittent duty cycles is relatively modest compared to other chemical systems. The modest effect of duty cycle on capacity delivered can be seen in the graph (Fig. 13).

The maximum recommended pulse drain for $LiFeS_2$ is based on the battery's ability to deliver high current over a range of 100 milliseconds to 2 seconds. The "AA" size can deliver up to a 3 Amp pulse. At these rates, it is important to consider heat generation by adjacent batteries and consider the effect on the PTC. This part will change from low to high impedance when activated during abusive conditions that cause a temperature rise. Actual testing is needed to determine the amount of additional service expected in pulse applications since there is no simple equation to accurately calculate the impact of duty cycle on service.

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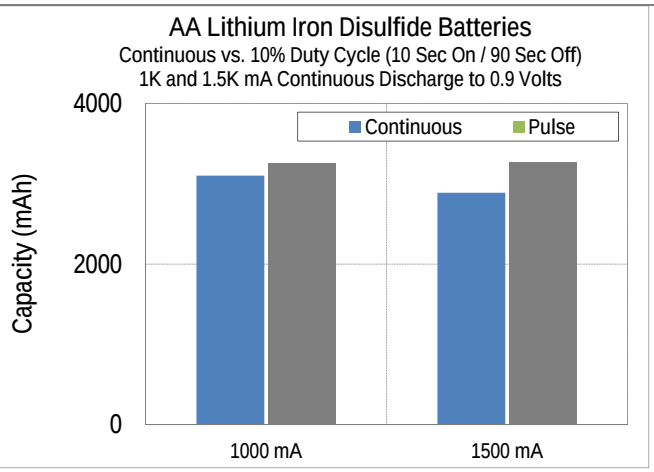
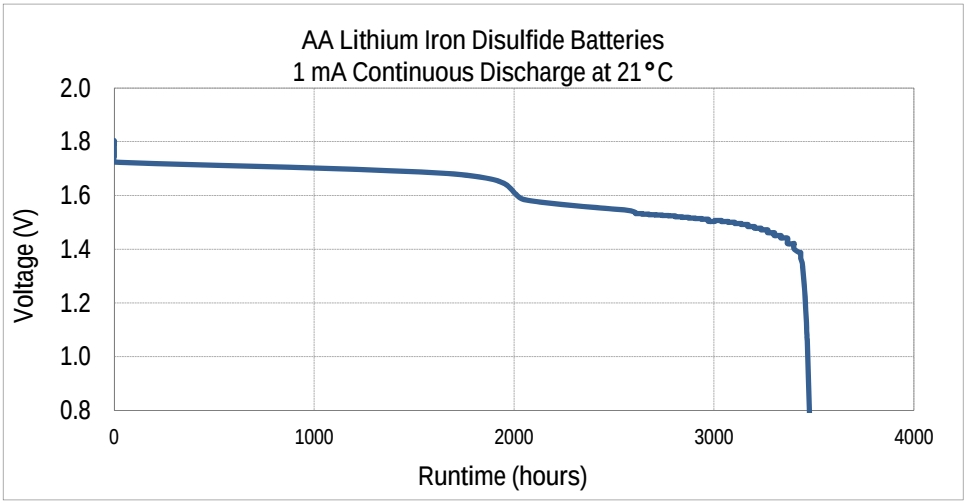


(Fig. 13) Effect of Duty Cycle

In ultra-low drain applications (i.e. currents in micro amps, where the battery is expected to run several months), the discharge curve has a distinct two stage profile. The first step occurs at slightly higher voltage (nominally 1.79V @ 21°C, dictated by thermodynamics) that increases with temperature and is nearly independent of depth of discharge. The second step occurs at a slightly lower voltage (nominally 1.7V @ 21° C) that decreases with temperature and is a function of depth of discharge. At low drain rates, the lithium iron disulfide battery will provide approximately full rated capacity over its lifetime.

The two stage discharge profile can benefit the device manufacturer as a method to implement fuel gauging in low drain applications. The discharge curve below shows the distinct plateaus where voltage, impedance, coulomb counting or combination of these methods could be used to determine depth of discharge needed to calculate remaining battery life. It should be noted that the lithium iron disulfide battery has a steep voltage drop off at the end of life (Fig. 14). Please contact your *Energizer*® sales representative for further information on this subject.



(Fig. 14) Two Stage Discharge

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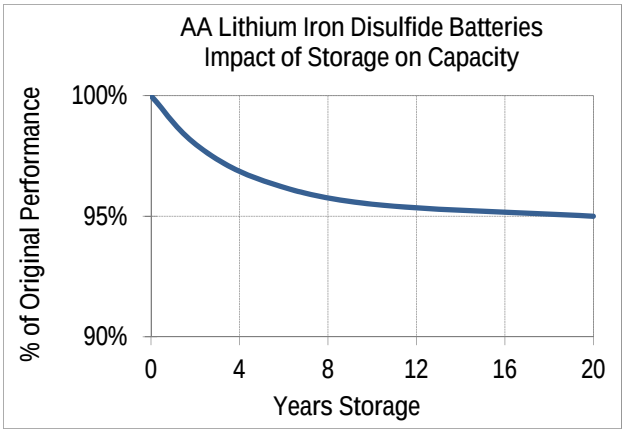

(Fig. 15) Impact of Storage

Shelf life can be defined as the time at which a battery will deliver approximately 95% of its original capacity (Fig. 15). The lithium iron disulfide battery will retain approximately 95% of its capacity after 20+ years of storage. Because of the very low level of impurities in the materials used and the high degree of seal effectiveness used with lithium batteries, the shelf life after high temperature storage is far better compared to aqueous systems. The recommended storage temperature for lithium batteries is -40°C to 60°C. Exposing lithium batteries to temperatures above 60°C can cause the insulating label to shrink and expose the battery's steel can to potential external short circuits. Cold temperatures will have little impact on shelf life.

Predicting battery shelf life is done in various ways. Typically, elevated temperature storage is used to accelerate those processes that cause degradation. This method is convenient, but is not always reliable because increasing cell temperature can introduce a new mode of degradation that is not present in batteries stored at lower temperatures. This could yield an underestimate of the true shelf life. Another method for predicting shelf life is microcalorimetry that measures the heat output from batteries and provides an estimate of the chemical changes occurring inside the battery. *Energizer*® has tested $LiFeS_2$ cells using all of these methods.

Testing / Care / Warnings:

The lithium iron disulfide construction incorporates many safety features and extensive quality checks during manufacture on each and every battery. The design includes two safety devices to provide protection against abusive conditions such as short circuit, charging, forced discharge and overheating.

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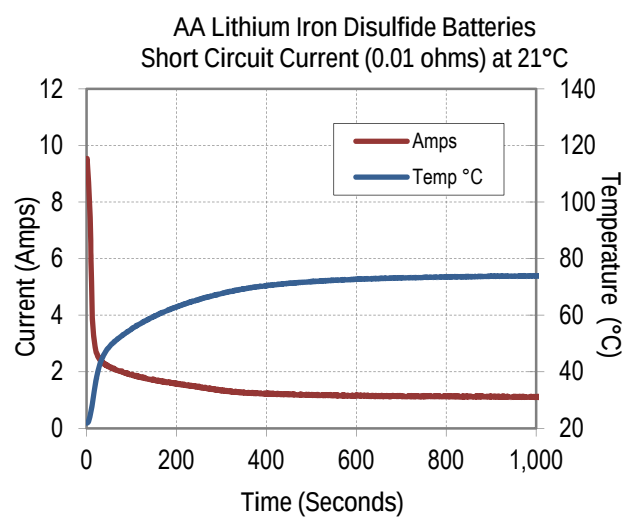
These two safety devices are a resettable thermal switch or PTC (Positive Thermal Coefficient) and a pressure relief vent. The PTC protects against electrical abuse scenarios by limiting the current when the PTC temperature exceeds 85°C. As the battery heats during abuse, the resistance of the PTC rapidly increases and significantly limits the amount of current flowing through the battery, thus allowing the battery to cool. When the PTC cools to below the activation temperature, its resistance returns to a normal level allowing normal battery use. The PTC is extremely effective in safely handling electrical abuse conditions. Here is an example of an "AA" size lithium iron disulfide battery subjected to a direct short showing that the PTC reduces the current within seconds to a safe level (Fig 16).

The PTC can rarely activate during non-abuse conditions, depending on how quickly the battery can dissipate heat generated from discharge. A combination of high discharge rate (which generates more heat) and high ambient temperature can cause the PTC to limit current.



(Fig. 16) Short Circuit Current

In addition, insulation within the battery compartment, proximity to adjacent batteries and neighboring electronic components can generate or retain additional heat. Intermittency, which is common for many applications, can greatly alleviate the internal heating affect.

During use, all batteries generate heat. On light loads the heat dissipates and is not noticeable, but on heavy drains the battery may become noticeably warm to the touch. This is expected and normal and also true of alkaline batteries. Extended exposure to heat may also cause shrinkage of the label. Label shrinkage can occur when the battery is exposed to extreme conditions and is not indicative of battery failure.

The vent mechanism operates at ~150°C and allows a controlled release of pressure thus preventing the battery from exploding in the event of abuse conditions, such as

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internal short circuits. This venting also limits the current the battery can carry and prevents additional heat generation.

The maximum continuous current drain for the "AA" size is 2.0 amps. Higher drain rates can be used for short periods of time. Because of the number of other variables involved, it is difficult to predict in advance whether lithium iron disulfide batteries can operate under extreme load conditions. In order to determine the highest pulse rate achievable, testing the batteries in the device under worst case conditions is recommended. While the PTC does impose some limitations on high rate applications for which lithium iron disulfide batteries are suitable, it is a critical element in ensuring that the battery is safe and protects the battery, the equipment and the user.
Although the safety mechanisms described above will limit the potential for battery failure due to abuse, there are additional handling considerations for the proper safe use of lithium iron disulfide batteries:

- Avoid potting or encapsulation as this obstructs the pressure relief vent. The vent is required to prevent excessive heat or pressure buildup if the battery is exposed to abusive conditions.

- Avoid charging as lithium iron disulfide batteries are not designed to be recharged.

- Use of pressure contact for batteries is recommended in the device compartment. If welded connections are needed, they should be made to the nickel-plated positive cap and the nickel-plated bottom using a capacitor discharge welder. Solder connections should be avoided because of the intense heat that needs to be applied to the battery.

- Battery labels insulate the battery to reduce the incidence of a potential direct short circuit or inadvertent charging. Battery compartment contacts and welded tab connections must not have sharp edges/burrs that could cut through the battery label especially adjacent to the positive terminal.

- Do not open battery, dispose of in fire, heat above 100°C (212°F), expose contents to water, recharge, install backwards, mix with used or other battery types. These conditions may cause personal injury.

- There is no risk of hydrogen generation with lithium iron disulfide batteries and they can be used safely in water tight applications.

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- Lithium iron disulfide batteries can safely undergo ethylene oxide or gamma radiation sterilization.

For additional information it is imperative to read the section "Design and Safety Considerations" to assure that other safety considerations are not overlooked.

Environmental Compliance and Global Directives:

Current information on environmental compliance, EU Battery Directive, REACH Directive Summary, RoHS-WEEE Directive and Compliance with Industry Standards can be reviewed on the *Energizer*®:

Technical Information Web Site under the "General Information" tab.

Shipping:

Shipping and transportation, including US DOT travelling with lithium battery guidelines, can be reviewed on the *Energizer*® Technical Information Web Site under the "General Information" tab.

There is also information on:

Lithium Battery Transportation for commercial aviation and IATA guidelines.

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