White Paper: A Primer on Primary Lithium Batteries

Introduction

The element lithium possesses fundamental properties that make it ideal for use as the anode in both primary and rechargeable batteries. Vendors have paired the popular lithium anode with a variety of cathode and electrolyte materials, resulting in the wide choice of different chemistries available today in the $1.5 billion primary lithium battery market.

This white paper highlights four existing types of primary lithium batteries and introduces a new one based on recent innovations in materials and manufacturing processes. Information about the basic properties, advantages and disadvantages, and typical applications is provided for each battery type, enabling the reader to compare all five.

The material is organized into three remaining sections followed by a brief conclusion. The first section explains why lithium is such a popular element for battery anodes. The second section contains reference information in summary form for each of the four existing battery types. The third section introduces a new Lithium/Carbon Fluoride battery, explaining how it employs advancements in nano-material science and manufacturing processes to customize or tune its cathode in various ways that optimize performance.

Why Lithium?

The popularity of lithium's use in batteries derives from its fundamental properties, which make it far superior to other metals as an anode material. Lithium's standard potential is over -3.0 V, exceeding sodium, magnesium and calcium. Lithium is also the lightest metal with a low density of only 0.54 g/cm^3. Indeed, at atomic number 3 (and having formed seconds after the Big Bang), lithium is the first element in the alkali metals group. Additional properties that make lithium ideal for batteries include its low resistivity, high ionization energy, low melting point and relative abundance.

These and other desirable properties combine to yield an impressive electrochemical equivalence of 3.86 Ah/g, readily exceeding all other contenders. Magnesium, calcium and sodium achieve electrochemical equivalences of 2.20 Ah/g, 1.34 Ah/g and 1.16 Ah/g, respectively. The only other metal that comes close to lithium's electrochemical equivalence is aluminum with a rating of 2.98 Ah/g. But aluminum's low standard potential of only -1.7 V presents a significant barrier to its use in batteries.

Despite beliefs to the contrary, lithium appears to be sufficiently abundant to meet the world's growing demand. As a fairly reactive element lithium is found in many materials, including various pegmatites, hectorite, continental brines, geothermal brines and oilfield brines. These source materials are currently mined in Argentina, Australia, Brazil, Canada, Chile, China, Portugal, Russian, Serbia, the United States (Nevada) and Zimbabwe. The tremendous demand for lithium has led to the search for new sources, with significant deposits being discovered recently in Bolivia and Mexico. The US Geological Survey (USGS) estimates that there is a reserve of 13 million tons of lithium worldwide, including 760,000 tons in the United States. With a global consumption of 25,400 tons of lithium in 2008, one-fourth of which was for batteries according to the USGS, there is an ample supply even in the face of growing demand.

Lithium is not without its issues, however. The largest deposits, totaling nearly three-quarters of the world's known reserves, exist in Bolivia, Chile, Argentina and China, which raises geopolitical concerns. Some in the United States, for example, claim the nation is simply trading its dependence on foreign oil for a dependence on a foreign metal with the dramatic increase in demand expected for Plug-in Hybrid Electric Vehicles (PHEVs) and large-scale storage in the Smart Grid. But until the next-generation of lithium-free battery chemistries becomes available, the demand for lithium will remain strong.

Existing Primary Lithium Battery Types

Although a lithium anode can be coupled with a variety of different cathode and electrolyte materials, four combinations lead the market today in primary lithium batteries: Lithium/Manganese Dioxide; Lithium/Sulfur Dioxide, Lithium/Thionyl Chloride and Lithium/Polycarbon Monofluoride. The summary information provided here is for comparison purposes only, and includes each battery type's basic properties, advantages and disadvantages, and typical applications. Note that because energy densities vary with the different form factors used for different applications, the ranges used here depict typical values for cells in applications requiring moderate to high rates of discharge.

Lithium/Manganese Dioxide

Lithium/Manganese Dioxide (Li/MnO_2) batteries are the current marketshare leader, estimated by Frost & Sullivan to be at approximately 50% in 2010, owing to their combination of low cost and safe operation compared to the other three existing primary lithium batteries.

Li/MnO_2 Basic Properties	Energy density of 150-250 Wh/kg and 500-650 Wh/l Operating temperature range of -20°C to 60°C
Advantages	Low Cost Safe operation
Disadvantages	Low gravimetric and volumetric energy densities Limited operating temperature range
Typical Applications	Low to moderate discharge in consumer electronics, military communications, transportation, RFID, automated meter reading, medical defibrillators, and memory backup

Lithium/Sulfur Dioxide

Lithium/Sulfur Dioxide (Li/SO_2) batteries provide a competitive price/performance ratio and can operate at very low temperatures, but safety concerns limit their use primarily to military and aerospace applications. The use of a liquid cathode also gives this battery an advantage in certain high-pulse applications.

Li/SO_2 Basic Properties	Energy density of 240-280 Wh/kg and 350-450 Wh/l Operating temperature range of -55°C to 70°C
Advantages	Low cost High pulse-power capability Low operating temperature
Disadvantages	Low volumetric energy and power densities Limited high operating temperature Suffers from passivation Safety concerns during high sustained discharge (causing overheating and pressure build-up) Generates toxic waste
Typical Applications	Military/aerospace communications

Lithium/Thionyl Chloride

Lithium/Thionyl Chloride ($Li/SOCl_2$) batteries afford improvements over Lithium/Sulfur Dioxide batteries in both operating temperature range and shelf life, giving this chemistry a nearly 30% marketshare in 2010, according to a Frost & Sullivan forecast. But safety concerns limit their use to only those applications requiring a relatively low discharge rate. Like Sulfur Dioxide batteries, Thionyl Chloride's liquid cathode gives it a similar advantage in high-pulse applications.

Li/SOCl$_2$ Basic Properties	Energy density of 250-400 Wh/kg and 600-900 Wh/l Operating temperature range of -55°C to 150°C
Advantages	High volumetric energy density High pulse-power capability Long service/shelf life Wide operating temperature range
Disadvantages	Low gravimetric energy and power densities Suffers from passivation Safety concerns during high sustained discharge (causing pressure build-up) Generates toxic waste
Typical Applications	Commercial/consumer electronics, military communications, transportation, RFID, automated meter reading, and memory backup

Lithium/Polycarbon Monofluoride

Lithium/Polycarbon Monofluoride (Li/(CF)$_n$) batteries have a similar volumetric energy density and longer shelf life than Manganese Dioxide batteries, and are just as safe to operate. Despite these advantages, however, this chemistry will achieve less than a 10% marketshare in 2010, according to Frost & Sullivan estimates, with continued growth expected only in medical and military applications.

Li/(CF)$_N$ Basic Properties	Energy density of 200-300 Wh/kg and 500-600 Wh/l Operating temperature range of -20°C to 60°C
Advantages	Long service/shelf life Safe operation
Disadvantages	Low gravimetric energy density Limited operating temperature range Poor performance at low temperatures
Typical Applications	Low to moderate discharge in consumer electronics, military communications, transportation, RFID, automated meter reading, medical defibrillators, and memory backup

The fact that four different types of primary lithium batteries continue to exist indicates that each has some compelling advantage, but that all also have one or more limitations. Sulfur Dioxide and Thionyl Chloride have relatively high energy and power densities, along with wide operating temperature ranges, but suffer from safety and environmental concerns that make then unsuitable for many applications. Manganese Dioxide and Polycarbon Monofluoride are safe and relatively benign environmentally, but fail to pack the power demanded by some applications. Recent innovations in the formation of carbon fluoride powder hold the potential to eliminate these traditional trade-offs.

Advanced Lithium Carbon Fluoride Batteries

The advanced Lithium/Carbon Fluoride (Li/CFx) battery maintains the benefits of high energy and power densities, wide operating temperature range and long shelf life found in Sulfur Dioxide and Thionyl Chloride batteries, while employing a solid cathode (with no heavy metals or other toxic materials) to eliminate the safety and environmental concerns. In addition, the advanced CFx battery possesses none of the operational problems exhibited by some other batteries, such as passivation.

Li/CF$_x$ Basic Properties	Energy density of >700 Wh/kg and 700-1000 Wh/l Operating temperature range of -60°C to 160°C
Advantages	High energy and power densities Very wide operating temperature range Long service/shelf life Safe operation
Disadvantages	Moderately higher cost but with improved price/performance
Typical Applications	Low to high discharge in portable electronics, military and search & rescue communications, industrial, transportation, RFID, automated meter reading, and medical defibrillators

Perhaps the most significant advancement found in these new Lithium/Carbon Fluoride batteries is the ability to customize or tune the cathode to meet an application's specific requirements. By altering how fluorine is introduced into the carbon structure at the atomic level during the manufacturing process, the battery's fundamental properties can be changed in ways that favor higher energy or power densities (see Figure 1). The customization process can also balance the battery's properties in other ways to optimize performance in a particular application.

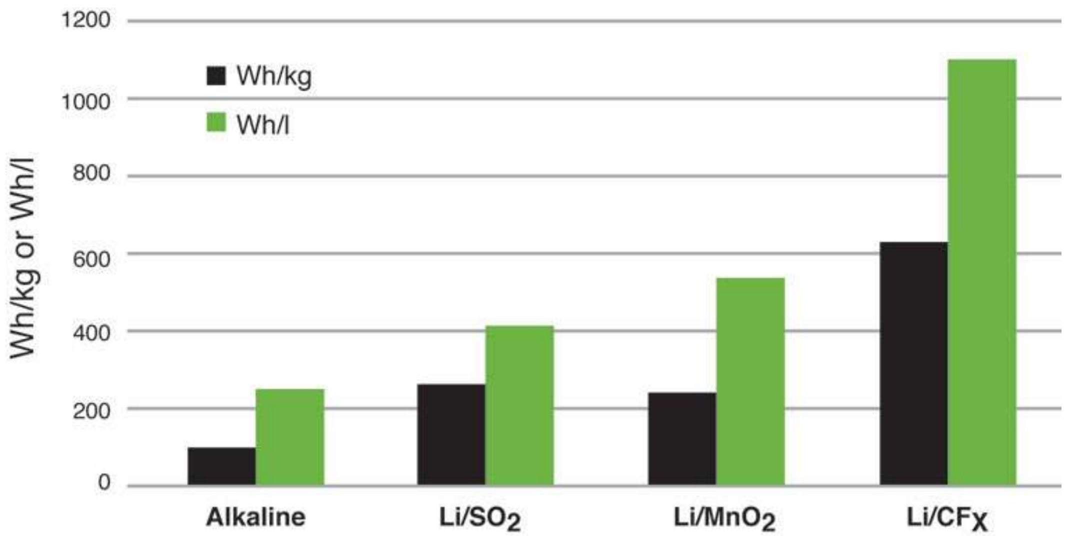

Figure 1: Here is a comparison of both gravimetric and volumetric energy densities for four different types of 2016 coin cells. As shown, the advanced CFx battery affords a significant improvement over both primary lithium and alkaline batteries.

Another major advantage of the advanced CFx battery is its ability to exceed all others in both power density and maximum safe current draw. Laboratory tests (see Figure 2) have demonstrated up to an eight times improvement in high-current applications, and a nearly two-times improvement in low-current applications. This makes the advanced CFx battery particularly well-suited for applications that require high sustained or pulse currents.

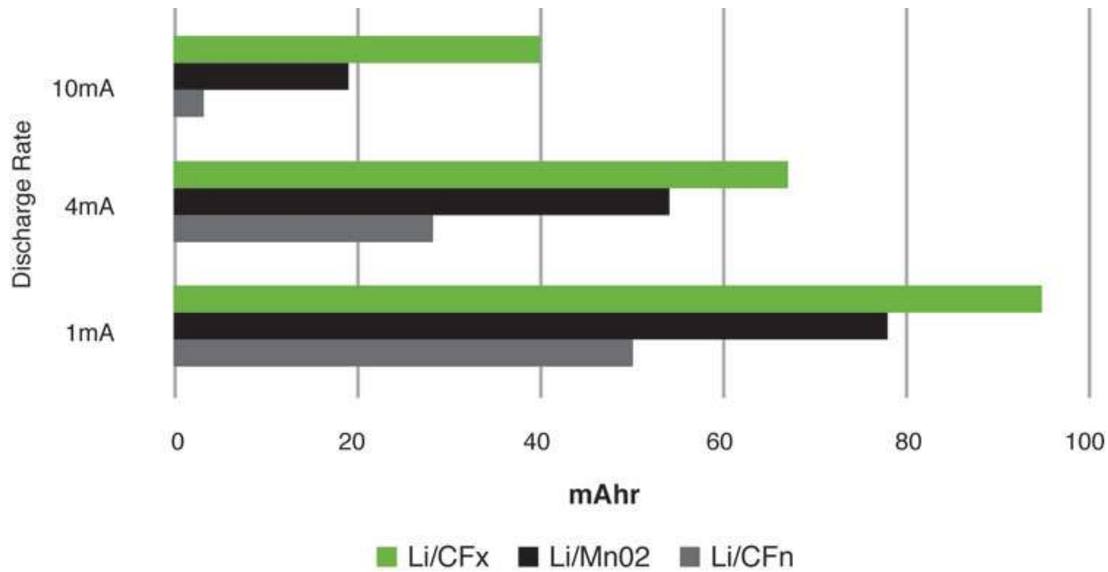

Figure 2: Here are the test results for available capacity at three different discharge rates (to 2.0V) for three different 2016 coin cells. As shown, the advanced CFx battery affords a significant increase in power density at low, moderate and high discharge rates.

Like the other lithium-based primary batteries, CFx batteries can be packaged in a variety of form factors, including coin, cell, film or prismatic. This enables CFx batteries to accommodate both standard sizes and customized packs, which may combine cells in series and/or parallel to satisfy specific needs.

Conclusion

The table below provides a summary comparison of key characteristics for all five types of primary lithium batteries.

	Li/MnO_2	Li/SO_2	$Li/SOCl_2$	$Li/(CF)_n$	Li/CF_x
Gravimetric Energy Density (Wh/kg)	150-250	240-280	250-400	200-300	>700
Volumetric Energy Density (Wh/l)	500-650	350-450	600-900	500-600	700-1000
Temperature Range (°C)	-20 to 60	-55 to 70	-55 to 150	-20 to 60	-60 to 160
Typical Shelf Life (Years)	5-10	10	15-20	15	15
Safe (High-rate Discharge)	Yes	No	No	Yes	Yes
Environmental Impact	Moderate	High	High	Moderate	Moderate
Relative Price/Performance	Fair	Good	Fair	Poor	Good

As this comparison shows, the advanced Lithium/Carbon Fluoride battery enjoys some significant advantages over all others. The single disadvantage at this time is its moderately higher cost. But when taking into account the increased performance based on higher energy and power densities, CFx offers a superior price/performance ratio than three of the alternatives. And over time, with additional advancements and growing economies of scale in manufacturing, Lithium/Carbon Fluoride can be expected to become the preferred choice for primary lithium batteries in a growing number of applications.

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About Contour Energy Systems

Contour Energy Systems (www.contourenergy.com) is an innovative portable power company commercializing customizable battery technologies for a wide range of cross-industry applications. Contour's next-generation battery systems are designed to deliver unprecedented improvements in energy and power density, and are capable of performing in extreme operating conditions at significantly improved costs. Founded through the collaboration of CalTech and CNRS, the French National Center for Scientific Research, the company combines expertise in nano-materials science, patented Fluorine-based battery chemistries and manufacturing processes to significantly advance the state of portable power. Headquartered in Azusa, California, Contour Energy is managed by a world-class team of battery industry leaders from CalTech, Energizer, Duracell, ConocoPhillips, Hewlett-Packard and Ultralife. The company is privately held with funding from CMEA Capital, Harris and Harris, Schlumberger and US Venture Partners.