Lithium-Sulfur Rechargeable Batteries: Characteristics, State of Development, and Applicability to Powering Portable Electronics

Frank B. Tudron, James R. Akridge, and Vincent J. Puglisi
Sion Power Corporation
Tucson, AZ 85747

Abstract

Lithium-sulfur technology developed at Sion Power forms the basis for a practical, high energy, light-weight, 2 V rechargeable battery system. The specific energy of this system exceeds that of state-of-the-art lithium ion by a factor of greater than 2-to-1, while the energy density stands at an equivalent level. Unit cell safety is improved beyond historical lithium metal rechargeables, due to the absence of dendrite formation in the sulfur chemistry. The combination of high energy and light weight make this an attractive technology for payload-critical applications.

Introduction

Lithium-sulfur (Li-S) rechargeable battery technology is capable of a specific energy of 400Wh/kg and an energy density of 425 Wh/liter. Further evolution of the technology has the potential to achieve a 25% improvement beyond these values. The specific energy exceeds currently used lithium ion rechargeables by a factor of over 2 to 1; the energy density is equivalent to lithium ion's. That is, Li-S provides the same runtime for a portable computer in less than half the weight or twice the runtime in the same weight while having a volume comparable to lithium ion. This performance level is obtained using sulfur's and lithium's high specific energies and novel electrode designs. Whereas the lithium ion active material couple yields about 500 Wh/kg ideally, the Li-S active material couple is more capable, yielding 2500 Wh/kg. Also, the ability to use plastic substrates for the sulfur cathode and vacuum deposition of lithium for the lithium anode provides weight savings not realized in other rechargeable technologies.

Prototype Li-S cells, operating at 250 to 300 Wh/kg and similar Wh/L values, demonstrate rate capability surpassing 3C and a temperature range of –60^{o}C to +60^{o}C. When charged and discharged at –10^{o}C to –20^{o}C at the 3C rate, the cell provides about 80% of the amp-hours and more than 75% of the watt-hours delivered at room temperature. At temperatures above 45^{o}C, the cell provides more capacity at a higher voltage yielding about a 10% Wh improvement relative to the room temperature value. A Ragone plot comparison shows that the Li-S cell will deliver higher specific energy than other rechargeable technologies such as LiIon, NiMH and NiCd at any discharge power. Self-discharge is $\leq$ 15% per month.

Safety is improved relative to lithium ion in that, unlike lithium ion, lithium dendrites do not form in Li-S cell. This is a result of the electrolyte/liquid cathode system employed. End of life capacity and voltage are determined by sulfur electrode fatigue and not by lithium electrode failure. Abuse testing at milestone design points during technology development has shown acceptable characteristics. The technology will meet safety standards. Guidelines are provided for prospective users to assess how this enabling technology will impact their applications in the future.

Background and Status

Sion Power's Li-S rechargeable battery development aimed to exploit the attributes of the chemistry and design possibilities to satisfy the power requirement of payload-sensitive applications. The chemistry's attributes are unique, exceeding all existing commercialized rechargeable chemistries in virtually all performance categories. In particular, its high specific energy (Wh/kg) directly addresses the prospective user's need for additional runtime for a given battery weight or equal runtime for less battery weight. For example, with this battery chemistry, the goal of achieving 8-hr runtime with an internal computer battery having a reasonable weight is possible. This will come with no energy density decrease, that is, the battery volume to provide a given runtime will not increase. This is possible due to the extremely high energy provided by the materials used in the Li-S cell when compared with the materials used in the lithium ion cell as illustrated in Figure 1. As shown, the theoretical energy provided by Li-S exceeds that provided by lithium ion by a significant margin both in specific energy and energy density. And as will be shown, the advantage in specific energy has already been realized in early prototypes. Figure 2 illustrates the evolution in specific energy that has taken place together with improvement in cycle life.

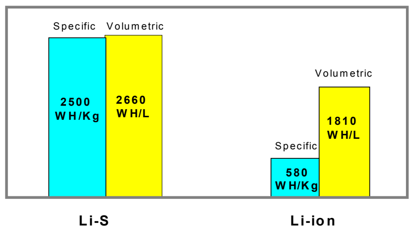

Figure 1: *Theoretical Energy Density Comparison*

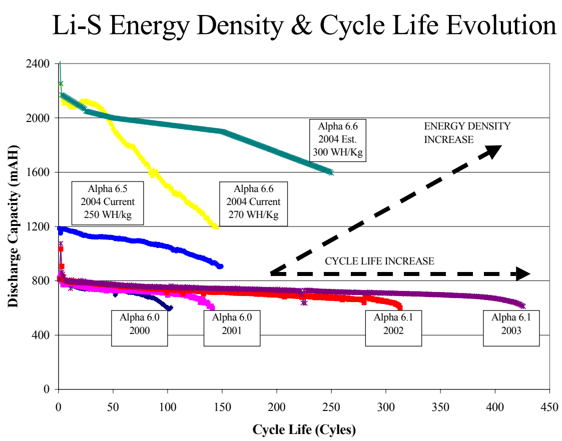

Figure 2: *Multi-generation Evolution of Li-S Performance*

It should be noted that with dramatic increases in specific energy, there is typically a corresponding decrease in cycle life, followed by a period of improvement and so on. Prototype cells in the range of 300 to 350 Wh/kg are now undergoing test. Energy density has been tracking the specific energy very closely to date, but is projected to surpass that value as geometric design factors assume a larger role relative to chemistry factors in any improvements obtained.

Figure 3 illustrates the electrochemical working of the cell. At the negative electrode, lithium is dissolved into solution on discharge

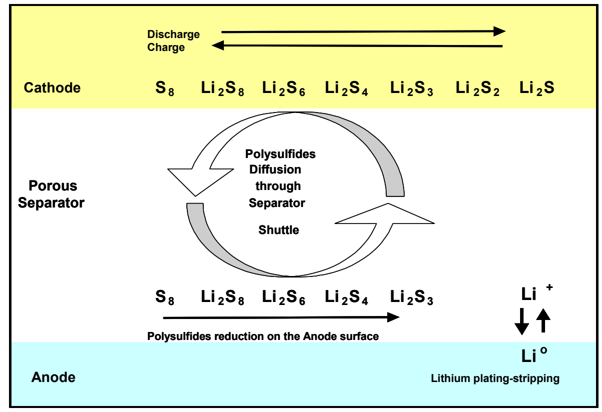

Figure 3: *Chemical processes in the Li-S rechargeable cell*

and plated out on charge. The sulfur chemistry is more complex in that a series of sulfur polymers are formed. Higher polymer states exemplified by Li_2S_8 are present at high states of charge, the charged form of the battery. Lower polymer states, exemplified by Li_2S, are present at low states of charge, the discharged form of the battery. Fundamental understanding of the sulfur electrochemistry has driven significant practical advances in specific energy and energy density. Sion Power has improved the sulfur utilization dramatically from about 46 to over 90 %. The result is that a gram of sulfur that was providing about 800 mAh now provides about 1500 mAh with no accompanying increase in weight or volume of the cell. This improvement is depicted in Figure 4.

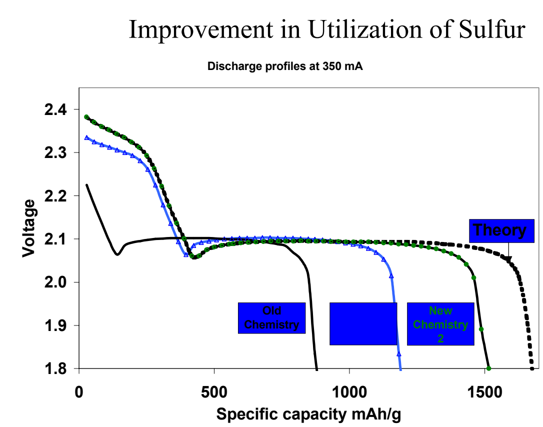

Figure 4: *Advances in sulfur usage-path to the present.*

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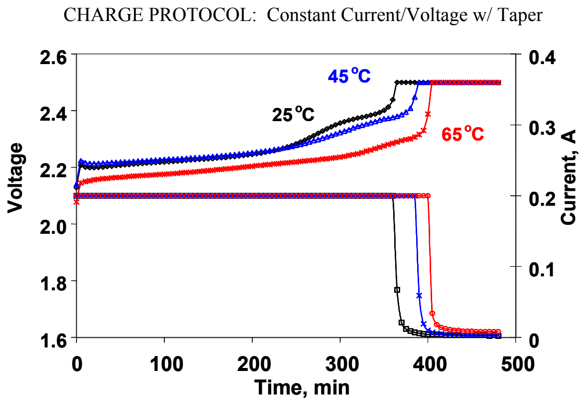

Figure 5: *Voltage-limited taper charge protocol*

Ease of charge and charge termination is of paramount importance in devising an application suitable battery system. Figure 5 shows an industry-accepted charge protocol using constant current charging terminated on reaching a pre-set voltage The initial charging can be followed by a tapering current, maintaining the pre-set voltage. This method is simple, inexpensive to implement and well understood by both battery and device manufacturers. Studies have shown that the lithium sulfur electrochemistry adheres to this accepted standard charge protocol.

As can be seen, the charge voltage increases during the charge until it ultimately exhibits a steep rise. In the test being illustrated, at the pre-set voltage, in this case 2.5 V, the current is tapered to lower values forcing the voltage to remain at 2.5. Further, this repeats itself in the same manner at all temperatures tested: 23, 45, and 65 °C.

After charging, the user typically does not immediately use the device: some extended and variable time may transpire before use. Tests are run on charged cells to characterize the self-discharge or charge retention over stand time. Figure 6 illustrates the voltage and ampere-hours delivered by the lithium sulfur cell following a charged stand time of over 8 days.

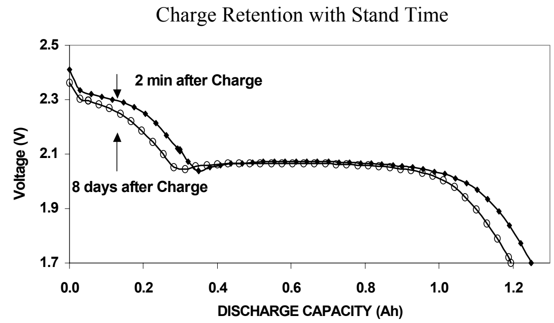

Figure 6: Charge retention of Li-S cells

As can be seen, the high voltage plateau is slightly depressed but the low voltage plateau is not affected. In addition the discharge capacity (Ah) is about 96% of that delivered with no stand. This performance is comparable with that of LiIon. The 3C rate discharge of the lithium sulfur cell at various temperatures is shown in Figure 7. An approximate 10% improvement in watt-hours is obtained when discharge is conducted at 65 C° versus 25 C°. This is the result of an increase in delivered ampere-hours plus an increase in the average voltage.

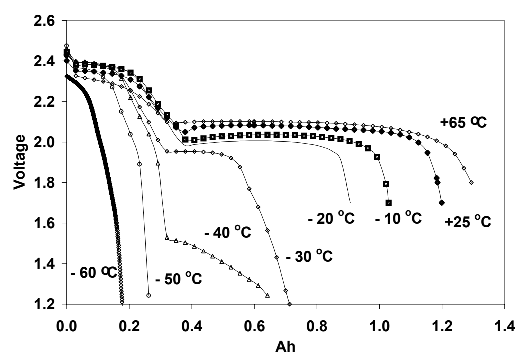

Figure 7: Temperature dependence of Li-S 3C rate discharge

Other characteristics of this technology include high discharge rate capability extending beyond 6 times the rated capacity and the ability to obtain useful energy at temperatures ranging from a low of minus 60 C° to a high of plus 60 C^o. The latter comes with the additional benefit of being able to perform the charge as well as the discharge at the test temperature.

These attractive features come together in designs currently exhibiting 300 to 350 Wh/kg and similar Wh/L values. Cycle life for these high specific energy and energy density designs is still low approaching 100 cycles but as shown in Figure 2 (*vide supra)*, historically this is typical. That is, as the energy within the cell is dramatically increased, cycle life becomes less until refinement of the design drives that characteristic back to acceptable values.

Application Testing

To study the operation of the lithium- sulfur battery, a Hewlett Packard TC1000 pen tablet was acquired for test. A smart battery pack was designed in the fall of 2003 using prototype lithium-sulfur cells with 250 Wh/kg specific energy (Figure 8).

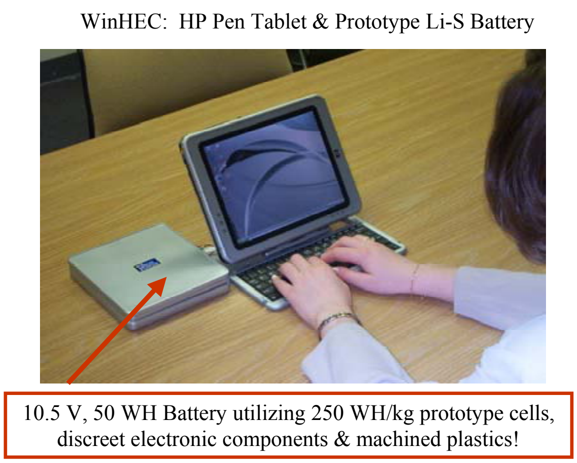

Figure 8: *Li-S smart battery pack configuration used for application testing*

Discreet electronic, components provided control, monitoring and safety circuits. Fuel gauging was not included but will be incorporated in a follow-on project. The plastics were machined parts. Although functionally sophisticated, the battery design was not optimized for either weight or volume nor was it possible to insert the battery into pen tablet battery compartment since the form factor was different. The battery consisted of 20 cells (4 parallel strings of 5 series-connected cells) and safety and control electronics. The battery provides 50 Wh (10.5 V, 4.8 Ah capacity). The LiIon original equipment battery with the computer delivers about 40 WH and is characterized by a rated voltage of 11.1 volts and a capacity of 3.6 AH. It consists of 6 cells arranged in 2 parallel strings of 3 cells.

Table 1 compares the prototype lithium sulfur battery with the target commercial product. A 100 Wh battery is projected for production using cells having a specific energy of 350 WH/kg.

Lithium Sulfur Battery Specification

Item	Prototype (1)	Production (2)
Voltage (V)	10.5	10.5
Capacity (AH)	4.8	8.8
WH/ battery	50	100
Cells (#)	20	20
Cell WH/kg	250	350
Cell WH/liter	265	400
Battery WH/kg		265 (3)
Battery WH/liter		320 (4)

Note 1: Prototype developed for WinHEC
Note 2: Initial production battery for pen tablet applications
Note 3: Projected based on current battery designs w/ cell contribution at 75 %
Note 4: Projected based on current battery designs w/ cell contribution at 80%

Table 1: *Comparison of the Li-S proto-type smart battery with its commercial counterpart*

Summary

Lithium-sulfur technology provides specific energy and energy density values far superior to any recharge-able battery technology in commercial production or on the research horizon. Charge retention with storage and charge termination protocols are con-sistent with the LiIon technology. Characteristics such rate capability and consistently high capacity delivery in the temperature range 23 ^{o}C to 60 ^{o}C are far superior to those of LiIon and thus can be device and application enabling.

Areas for additional advancement are: increasing specific energy and energy density; increasing cycle life; continuous improvement in safety of cells and battery packs; and finally, exploiting lithium sulfur's unique chemistry for battery fuel gauging.

Acknowledgement

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