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Arthur D Little

**Survey of
Rechargeable
Battery Technology**

**Report to
Lawrence Livermore
National Laboratories**

**Subcontract B235246
between
The Regents of the University
of California
and
Arthur D. Little, Inc.**

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- Exhibit 2.1:** The application imposes demanding performance requirements which cannot be met by existing commercial battery technologies
- Exhibit 2.2:** A near-term demonstration in which the diurnal cycle is "broken" will require a minimum of 175 Wh/kg
- Exhibit 3.1:** In addition to the LLNL performance requirements, we imposed screening criteria associated with the prospects for practical implementation.
- Exhibit 3.2:** Several candidate high energy density systems can be identified (Aqueous).
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- Exhibit 3.4:** A methodology to estimate achievable energy density for candidate systems incorporates successive consideration of the required parasitic for the batteries.
- Exhibit 4.1:** Aqueous systems provide generally higher "packaged" specific energy ratios (reflecting maturity) but few can meet the specific energy requirement even at the theoretical level.
- Exhibit 4.2:** At the cell level, specific energy greater than 300 Wh/kg can be achieved for a pure SPE system.
- Exhibit 5.1:** The basic lithium-solid polymer electrolyte design includes thin layers of "composite" cathode (50 to 75 μm), of solid polymer electrolyte (25 to 50 μm), and of a metallic lithium foil anode. This assembly is called "laminate".
- Exhibit 5.2:** Cylindrical cell design (75 Ah) and cell assembly offers flexibility for the assembly of 60 kWh batteries in this concept, and limits parasitics.

- Exhibit 5.3: Cylindrical cells can be mounted in the spar as sub-assemblies in a combination compatible with voltage/current, charge control protocol, and provide easy access for maintenance and replacement.
- Exhibit 5.4: Analysis of cell design trade-offs indicates that specific energy greater than 200 Wh/kg could be achieved, without requiring cathode coating width greater than what has been demonstrated to-date.
- Exhibit 5.5: In a sub-unit, the number of cells and their dimensions can be optimized to reduce the probability of a catastrophic mission interruption caused by a unit cell and/or a sub-unit failure.
- Exhibit 5.6: Battery system specific energy, based on an advanced Li-SPE configuration and conventional cell "packaging" could reach 180 Wh/kg.
- Exhibit 5.7: Battery system specific energy, based on an advanced Li-SPE configuration and novel cell "packaging" could reach over 210 Wh/kg.
- Exhibit 7.1: The effective charging period is reduced because of the decreased power of the PV during the early and last hours of sunlight.

1.0 Executive Summary

Arthur D. Little has reviewed rechargeable battery technology options available to Lawrence Livermore National Laboratories (LLNL) for a specialized application in un-manned high altitude aircraft. Consideration was given to all rechargeable battery technologies that are available commercially or might be available in the foreseeable future.

The LLNL application was found to impose very demanding performance requirements which cannot be met by existing commercially available battery technologies. The most demanding requirement is for high energy density. The technology that comes closest to providing the LLNL requirements is silver-zinc, although the technology exhibits significant shortfalls in energy density, charge rate capability and cyclability. There is no battery technology available "off-the-shelf" today that can satisfy the LLNL performance requirements.

All rechargeable battery technologies with the possibility of approaching/meeting the energy density requirements were reviewed. Key areas for focus included the state-of-the-art, as well as commercial availability. Vendor interviews were carried out for all relevant technologies. A large number of rechargeable battery systems have been developed over the years, though a much smaller number have achieved commercial success and general availability. The theoretical energy densities for these systems are summarized in exhibit 1.1. It should be noted that a generally useful "rule-of-thumb" is that the ratio of packaged to theoretical energy density has proven to be less than 30%, and generally less than 25%. Data developed for this project confirm the usefulness of the general rule. However, data shown for the silver-zinc (AgZn) system show a greater conversion of theoretical to practical energy density than would be expected due to the very large cell sizes considered and the unusually high density of the active materials.

In carrying out this work, we note that energy density values which can be found in the literature are often over-stated from the point-of-view of the LLNL application. The data most often refer to real or prospective single cells. Thus, the energy density for the subject technology is degraded significantly in appropriately packaged batteries (as opposed to in isolated cells). It is also common, especially for the polymer electrolyte technologies, that single cell values are often unrealistic "best case" projections.

Exhibit 1.1: Survey of Theoretical and Practical Energy Density for a Variety of Candidate Rechargeable Battery Systems.

Only an "advanced" lithium metal-solid polymer electrolyte rechargeable battery technology can provide the specific energy (>200 Wh/kg) in packaged batteries that is required for the LLNL application. In contrast, today's gelled electrolyte polymer electrolyte battery technology sacrifices energy density and cyclability. Although the latter may present a near-term approach to break the diurnal cycle, a major development effort would be required. Such an effort may not be easy to justify given the long term limitations of the technology. A focussed development effort involving true, solvent-free solid polymer electrolyte battery technology is the best approach to provide the battery technology required for this application. Estimates of possible energy density for such a system are in the range of over 220 Wh/kg in a packaged battery could be achieved.

Arthur D. Little has considered various packaging options to achieve the desired battery, and has developed a "most favorable" concept. Novel packaging is required to reduce the load on the battery associated with parasitic components. The concept is based on a variety of cell design and battery design tradeoffs, and involves development of spar-loadable cell clusters (not necessarily man-rated) that provide over 220 Wh/kg fully packaged and over 300 Wh/kg at the cell level.

2.0 Battery Design Targets

In carrying out this assessment, Arthur D. Little utilized a series of performance specifications provided by LLNL. The most critical of those requirements are summarized in Exhibit 2.1. As will be seen, the requirements summarized in Exhibit 2.1 cannot be met by existing commercial battery technologies.

BATTERY REQUIREMENTS	
Specific Energy (Wh/kg)	> 200
Cycle Life (Deep Discharge)	100-300
Recharge Time (h)	< 8
Capacity (kWh)	≥ 60

Exhibit 2.1: The application imposes demanding performance requirements which cannot be met by existing commercial battery technologies.

Given that the load conditions for a battery may change in the future as a result of design decisions and/or technological improvements, it was important to maintain some flexibility regarding the comparison of each battery technology to the performance hurdles. Such a philosophy was followed throughout the assessment. Thus, all technologies that might be close to the targets were considered and are summarized below. In addition, specific technical targets associated with breaking the diurnal cycle were considered and are summarized in Exhibit 2.2.

Parameter	Short term	Long term
Specific Energy (Wh/kg)	175	> 200
Weight (kg)	68	225
Cycle life (at 100% DOD)	> 50	50-500
Total usable capacity (kWh)	12	60
Operating temperature (°C)	-10 to 75	-10 to 75
Operating pressure (atm)	.03 to 1	.03 to 1

Exhibit 2.2: A near-term demonstration in which the diurnal cycle is "broken" will require a minimum of 175 Wh/kg.

The requirements summarized in these two exhibits represent the criteria that had the greatest impact on selection of candidate battery technologies.

3.0 Survey of Battery Technology Candidates

All rechargeable battery technologies presently available commercially, or under significant development were considered as initial candidates for the application. The only rechargeable technologies that were more or less ruled out from the outset were:

- Nickel-cadmium, with specific energy of approximately 40 Wh/kg
- Sealed lead acid, with specific energy of approximately 35 Wh/kg, and
- Nickel-metal hydride, with a specific energy of approximately 70 Wh/kg.

It was noted that the LLNL application required a battery that was roughly the size of an electric vehicle battery. It was therefore not surprising that many of the candidate technologies have been under development for such applications.

The application requirements push the limits of energy density and available cell sizes for all candidate battery technologies. Accordingly, it was important in this work to extrapolate available data and to interpret available data for the various candidate systems. Estimates of impact of scale up on cell performance characteristics were made. In addition, certain assumptions regarding the use of lightweight cell/battery packaging were made in order to estimate the potential maximum energy density under the most favorable, but still realistic conditions. As summarized below, a methodology was developed to examine and to estimate the upper achievable limits of energy density.

In addition to the LLNL performance requirements, Arthur D. Little imposed an additional set of screening criteria associated with the prospects for practical implementation of the various battery technologies being considered. These criteria, summarized in Exhibit 3.1, were used as a test of practicality, and the ease of potential implementation.

ADDITIONAL SCREENING PARAMETERS	
Specific Energy	How close to target
Availability	Maximum cell and battery size
Thermal Management	Additional system complexity
Cycle Life	How close to target
Conformability	Adapt to volume constraints
Battery Optimization	Cell to battery tradeoffs

Exhibit 3.1: In addition to the LLNL performance requirements, we imposed screening criteria associated with the prospects for practical implementation.

The battery technologies that were considered in this assessment are summarized in Exhibit 3.2. Additional data in this exhibit identify suppliers/developers of each technology, the largest cell size available and key issues associated with the technology.

System	Supplier/Developer	Typical Size	Key limiting Factors
Aqueous Based, Ambient Temperature			
Ag/Zn	Eagle Picher	> 300 Ah	• Charge acceptance
Zn/O ₂	1Matsi/2AER/3Demi	15 Ah	• Cycle life/electrolyte management

- 1 Matsi is located in Atlanta, Georgia
2 AER Energy is located in Atlanta, Georgia
3 DEMI is located in Santa Barbara, California

Exhibit 3.2: Several candidate high energy density systems can be identified (Aqueous).

System	Supplier/Developer	Typical Size	Key limiting Factors
Non-Aqueous Based, High Temperature			
Na/S	Chloride Silent Power/Eagle Picher	55 Ah	• 350°C
Na/NiCl ₂	1Harwell/Beta Res./2CSIR & 2Zebra	>140 Ah	• 250°C
LiAl/FeS _x	Argonne Nat. Lab/3SAFT	-	• 400-450°C
Non-Aqueous, Ambient Temperature			
LiC/Liquid/LiCoO ₂	Sony	1 Ah	• Low specific energy
Li/Liquid/TiS ₂	4JPL	1 Ah	• Low specific energy
Li/Liquid/LiCoO ₂	5Alliant/3Saft	6 Ah	• Low cycle life
Li/SPE/MO _x	Valence/Hydro-Quebec/1Harwell	≈ 5 Ah	• Un-proven technology

- 1 Harwell, also known as Atomic Energy Agency is located in Oxfordshire (UK)
2 CSIR & Zebra represent a South-African consortium
3 SAFT America is the US-based subsidiary of SAFT (France)
4 JPL is the NASA Jet Propulsion Laboratories in Pasadena, California
5 Alliant Techsystems (formerly Honeywell) is located in Horsham, Pennsylvania

Exhibit 3.2 (continued): Several candidate high energy density systems can be identified (Non-Aqueous).

The first screen which was used to evaluate the various battery technology options focussed on the most challenging requirement; namely gravimetric (or specific) energy density. A useful test for the candidate systems is to recognize that (1) a variety of theoretical energy densities ranging from less than the target value (e.g., for lead-acid) to nearly 200 Wh/kg, and (2) that the conversion of theoretical energy to practical energy density in realistic hardware has historically always been less than 30%, and more typically less than 25%. This ratio holds because it is necessary to package the active materials of a battery to make a practical battery. The packaging materials include separators, current collectors, electrolyte, cell vents and tabs, a can, and other components. All these components have no intrinsic energy value and are therefore parasitic. Exhibit 3.3 summarizes the situation for the rechargeable battery technologies under consideration for the LLNL application.

The achieved energy density for silver-zinc (AgZn) shown in Exhibit 3.3 is noteworthy and unusual. The ratio of packaged energy density to theoretical energy density is over 40%. This situation arises because 1) very large cell sizes were considered for these calculations, and 2) the density of the active materials is unusually high in this battery chemistry.

Fuel cell data based on: Regenerative Fuel Cells for High Altitude Long Endurance Solar Powered Vehicles, F. Mitlitsky, N.J. Colella, B. Myers and C.J. Anderson submitted to IECEC, Atlanta, GA, August 8-13, 1993.

Theoretical energy density for fuel cell is 3660 Wh/kg.

Exhibit 3.3: The ratio of packaged to theoretical energy density has proven to be less than 30% (which suggests one useful screening approach).

Exhibit 3.3 (continued): The ratio of packaged to theoretical energy density has proven to be less than 30% (which suggests one useful screening approach).

Nevertheless, the above rule-of-thumb is useful, and has some interesting consequences. If a target energy density corresponds to more than 30% of the theoretical energy density for the subject battery technology, then it follows that (1) in the extreme, the developer is claiming superiority in cell engineering relative to all previous designers of batteries (In our experience, many developers of battery technology will adjust their estimates of energy density downward when confronted with these data, (2) a specific strategy of minimal packaging is being pursued.

Since it was anticipated that the strategy of minimal packaging might be crucial for this assessment, the methodology summarized in Exhibit 3.4 was developed. This methodology explicitly examines the impact of successive processes of fabrication of a complete battery. In subsequent assessments, we utilized data summarizing dimensions, densities and electrochemical capacities to assess potential energy densities for each form of the candidate battery technologies.

Exhibit 3.4 shows that the theoretical energy density for any battery system occurs when equal electrochemical quantities of both positive and negative electrode active materials are used. Since no battery will function under these conditions, e.g., since electrolyte and minimal packaging materials are required, this energy density is not available in practical hardware. In fact, as indicated above, the theoretical energy density is substantially degraded in order to achieve practical cells.

Exhibit 3.4: A methodology to estimate achievable energy density for candidate systems incorporates successive consideration of the required parasitic for the batteries.

The first level of "degradation" of theoretical energy density occurs for the so-called "stoichiometric" complete cell. Thus, the addition of electrolyte, separator, current collector in a balanced cell must occur before current can be drawn from a cell. The cell may still not be practical, and is still not packaged, but the process of adding these mandatory components results in a degradation of the theoretical energy density that can be calculated.

The next "degradation" involves the design of a practical cell that cycles well, and is usually not electrochemically balanced. Usually it is necessary to utilize non-stoichiometric quantities of the active materials in a cell in order to facilitate cycling.

Finally, the technology is packaged in commercial hardware. Again, a significant degradation of theoretical energy density results. As will be seen in subsequent analyses, it is this final step (in Exhibit 3.4) that can be modified under certain circumstances to reduce parasitic loadings and to enhance prospects for high energy density with any given battery system.

4.0 Analysis of Battery Technology Candidates

As was illustrated in Exhibit 3.2, a variety of candidate battery technologies were identified. A subset of the most viable technologies included:

- Silver-zinc, which is commercially available today
- Rechargeable zinc-air, or zinc-oxygen, under development by several organizations
- Various high temperature chemistries, including sodium-sulfur, sodium-nickel chloride, and lithium/aluminum-iron disulfide
- Rechargeable lithium, employing liquid electrolyte and using either lithium-ion anodes or lithium metal anodes
- Rechargeable lithium-solid polymer electrolyte (SPE)-metal oxide. Today's state-of-the-art polymer electrolyte battery utilizes gelled electrolyte (e.g., based on 70% or more solvent content) and involves significant performance tradeoffs. However, the next generation polymer electrolyte battery technology will avoid these tradeoffs, and will have a significantly improved prospect of satisfying the LLNL performance requirements.

When considered as a group, it is clear that the aqueous electrolyte battery technologies generally provide a high level of conversion of theoretical energy density to practical energy density (which may simply reflect the relative maturity of these systems). However, few of these technologies can meet the specific energy requirement for the LLNL application even at the theoretical level. The situation is summarized in Exhibit 4.1.

4.1 Silver-Zinc

The silver-zinc system has the virtue that it is the system that is closest to meeting the LLNL performance requirements and is actually available in commercial hardware in cell of appropriate sizes. For example, a 15 kWh (28 volts, 555 Ah) silver-zinc battery is available from Eagle-Picher. This battery has an energy density approaching 160 Wh/kg, although this energy density is available only in early cycles and at low discharge rates.

The usefulness of these batteries is limited since:

- The maximum specific energy density specified for the technology is not available at the operating conditions that are relevant for the LLNL application. The discharge rate required is higher than the recommended discharge rate for the technology. The stated energy density is valid for only the first discharge cycle.
- The recommended recharge rate for the technology is approximately 48 hours, clearly inappropriate for this application.
- The technology has a low charge/discharge round trip efficiency, less than 80%.

Exhibit 4.1: Aqueous systems provide generally higher "packaged" specific energy ratios (reflecting maturity) but few can meet the specific energy requirement even at the theoretical level.

- There is a high rate of capacity fade for the system during cycling. After 45 cycles, the system delivers less than 60% of its initial capacity.
- The technology has limited cycle life, typically 100 cycles or less.

4.2 Rechargeable Zinc-Air (Zinc-Oxygen)

The zinc-air system offers one of the highest possible energy densities for a battery system. In the last few years, several activities have been focussed on attempting to make the system rechargeable. In principle, this goal involves definition of a reversible air cathode which is suitably catalyzed for both charge and discharge reactions. At the zinc electrode, the longstanding problem of cycling of zinc in alkaline solution must be addressed.

In most cells, considerable excess zinc may be used to facilitate cycling. This design approach results in a de-rating of the cell capacity somewhat, since the limiting electrode capacity is not 100% discharged each cycle.

The three major developers of the rechargeable zinc-air (zinc-oxygen) system in the U.S. are AER Energy Systems (Atlanta), DEMI (Santa Barbara) and MATSI (Atlanta). There are variations of design and chemistry in each of these approaches, but each was considered in the analysis.

The usefulness of rechargeable zinc-oxygen for the LLNL application is limited because of several practical problems in extended cell operation:

- Poor cycling of the zinc electrode requires cell designs with a large excess of zinc, typically reducing the available zinc capacity by a factor of two or more
- Electrolyte management is difficult. Since the cell in most designs must breathe oxygen from the external environment, cell dry-out occurs unless ambient air is highly humidified
- The technology exhibits a high rate of capacity fade, often as high as about 0.5% per cycle. Significant capacity is foreseen even in closed systems (as seen by LBL in their well known zinc work)
- The system exhibits relatively low round-trip efficiency, typically less than 75% and can be as low as 60%.

4.3 Sodium-Sulfur

The sodium-sulfur battery technology has received major development attention for the last two decades for aerospace and traction applications. It operates at about 350 degrees C, and is the most highly developed of the high temperature battery technologies.

The sodium-sulfur system is available for batteries of multi-watt-hour capacity, for example from Eagle-Picher. However, for the LLNL application, the technology has limited usefulness because of several factors:

- The maximum specific energy which can be foreseen for a cell is of the order of 200 Wh/kg, excluding thermal management packaging. The need for thermal management further reduces the ability to achieve sufficiently high specific energy
- The high operating temperature is a concern for the LLNL application. Thermal management electrical loads, and a significant heat signature detract from the viability of the technology
- Cycle life for practical cell hardware of high specific energy is still not demonstrated, and must be regarded as unproven

4.4 Sodium-Nickel Chloride

The sodium-nickel chloride battery system, sometimes referred to as the zebra system, operates at high temperatures also, so that many of the concerns summarized above for sodium sulfur apply to this system as well. The technology is available in multi-watt-hour cells.

The sodium-metal chloride system has limited usefulness for the LLNL application because:

- The system has a low specific energy relative to the LLNL requirements. Typical energy densities ranging from 85 Wh/kg to 140 Wh/kg are observed. Cells and batteries in the capacity range 125 Wh to 30 kWh have been made.
- The need for thermal management reduces the probability to realize the high specific energy needed for this application.

4.5 Lithium aluminum-iron disulfide

The lithium aluminum-iron disulfide battery technology is another of the high temperature battery systems, operating above 400 degrees C. It can provide specific energy for single cells of the order of 150 Wh/kg, and has good retention of capacity upon cycling. The technology has limited usefulness, however, given its relatively low energy density, its high operating temperature and the requirement to add a significant quantity of thermal management hardware. The available energy would be reduced by battery formation, and further by thermal management components.

4.6 Lithium-ion

The lithium-ion battery technology has received considerable attention in the last few years. A large number of companies have been active in developing the technology, most notable Asahi Chemical and Sony, with the latter bringing cell/battery hardware to the market in 1991. The technology can provide extensive cycle life and improved energy density relative to other consumer technologies such as nickel-cadmium.

For the LLNL application, the lithium-ion technology has limited usefulness. Its specific energy in small cells is only in the range of 80 to 100 Wh/kg, and is not available in large cell configurations at the present time.

4.7 Rechargeable Lithium-Metal Oxide

Rechargeable lithium battery technologies employing any one of several intercalation cathodes were also considered as candidate battery technologies. The most typical cathode material is a metal oxide, most often of manganese, cobalt, nickel or vanadium.

Energy densities of approximately 120 to 170 Wh/kg have been obtained in small cell configurations, with cycle life typically in the range of 50 to 150 cycles. Many factors which limit the cyclability of this system and result in significant capacity fade during cycling are related to the nonaqueous electrolytes employed, and are found in gelled polymer electrolyte systems as well. The energy density for this system is low relative to the LLNL targets, and would be degraded further in complete batteries.

The largest demonstrated cells are of the order of 18 Ah. Larger cells of the order of 100 Ah are probably at least two years away.

4.8 Lithium-Titanium Disulfide

The lithium-titanium disulfide system generally has many of the same characteristics as the rechargeable lithium-metal oxide systems described above. It has recently demonstrated specific energy density of approximately 130 Wh/kg in small cell configurations, and cycle life of more than 500 cycles.

Recent data generated at the Jet Propulsion Labs using their version of the technology illustrated that as many as 900 cycles could be obtained, though at just 50% depth-of-discharge (DOD). This DOD corresponds to just 65 Wh/kg. Discharge rates of C/5, and recharge rates of C/10 were used. At 100% DOD, approximately 300 cycles can be achieved, corresponding to about 90% of the rated capacity at a C/5 discharge rate. Nevertheless, lithium cyclability in these electrolytes remains an issue. The lithium electrode figure-of-merit (FOM) is very similar to that observed in other rechargeable lithium systems, and is approximately 65 to 70.

4.9 Lithium-Solid Polymer Electrolyte-Metal Oxide

The lithium-solid polymer electrolyte (SPE)-metal oxide technology is the only technology which appears capable of satisfying all the mission requirements of the LLNL application. However, it is important to make a clear distinction between today's typical SPE technology employing a gelled electrolyte, and the potential performance of a solvent-free solid polymer electrolyte.

Today's gelled electrolyte technology suffers from many of the same deficiencies summarized above for rechargeable lithium-metal oxide systems. The technology falls short of the specific energy and cycle life targets. In addition, large cells suitable for the LLNL mission are not available commercially, and very few have ever been made. Furthermore, large cells employing today's SPE technology, and perhaps all cells employing SPE, should be considered an unproven technology.

Despite its unproven status, it seems clear that the technology is attracting considerable attention and support. The United States Advanced Battery Consortium (USABC) has targeted the development of 20 to 40 kWh batteries based on the technology in the next few years. In addition, the Hydro-Quebec development program, which so far is the largest and most advanced development effort involving SPE batteries, has established an objective for 1994 of a 2 kWh battery with 93 Wh/kg and 115 Wh/l.

The prospects for a "next generation" polymer electrolyte technology employing a true polymer electrolyte are much more promising. This advanced SPE overcomes the limitations of today's gelled SPE with respect to key LLNL mission requirements. Thus, while gelled technology requires large excess lithium, and sacrifices energy density as a result, the next generation approach may not. Similarly, gelled technology will have limited cycle life very similar to that observed for liquid electrolytes. Next generation technology may not have these limitations. Finally, gelled technology will limit some of the packaging options due to the volatile components. Next generation technology which is truly solid state without volatile components may not present these limitations.

The SPE technology could be scaled up in an aggressive development program, although there would be significant risk and uncertainty. The parameter most likely to be negatively impacted by a rapid development program would be cycle life. While 50 to 100 cycles could be achieved rapidly, achievement of 100 to 500 cycles would require improved materials and components. Further improvement to more than 500 cycles would require fundamental improvements.

Gelled technology could be the subject of a major development program, but would represent only an interim solution given the inherent limitations on energy density and cycle life. Accordingly, it may be difficult to justify major development efforts for the gelled technology, and more appropriate to focus on the advanced approaches.

Our calculations indicate that cell capacities over 300 Wh/kg can be achieved for a pure SPE system. Exhibit 4.2 summarizes the progression from cathode material to a functional battery (compare with Exhibit 3.4. We will return to this issue in a more careful consideration of the prospects for minimal packaging concepts. Exhibit 4.2 indicates that a functional cell with energy density of about 330 Wh/kg would be possible.

An advanced polymer electrolyte technology which employs solvent-free solid polymer electrolytes can surpass lithium-liquid electrolyte and lithium-gelled electrolyte technologies in several ways. There are several important reasons for this conclusion. To achieve the highest possible energy density and meet the specific energy requirement, one wants to use lithium metal and a high voltage cathode material. A high energy density cathode material can be used only if the electrolyte has a wide electrochemical stability window - wider than any of the liquid or gelled electrolytes known to-date.

In addition, "novel" packaging approaches which reduce parasitic losses should also be considered, and might represent the key to obtaining the specific energy density values desired for the LLNL application. Ideally, one wants to use the minimum possible packaging to contain and ship the battery, which might not necessarily be man-rated. Concepts of minimal packaging are facilitated by the use of solvent-free polymer electrolyte technologies.

Exhibit 4.2: At the cell level, specific energy greater than 300 Wh/kg can be achieved for a pure SPE system.

5.0 Arthur D. Little Suggested Concept

Arthur D. Little has developed a novel "minimum packaging" concept to achieve the highest possible specific energy for a battery system. The approach recognizes the demanding nature of the LLNL targets for energy density, and that alternative approaches to traditional battery packaging are worth considering for this application.

The major feature of the approach is to utilize the minimum possible battery packaging consistent with containment, shipping and handling requirements, and extended life. Novel packaging involves the use of multi-layer plastic-metal thin film laminates which are impermeable to H_2O , O_2 , and N_2 . This approach allows a lowering of the overall parasitics associated with packaging. The packaging recommended for such an approach is diminished from what would ordinarily be provided for commercial cells, and the cells may not necessarily be man-rated. With this approach, we estimate that energy density might reach 250 Wh/kg for the advanced SPE versus about 150 Wh/kg for today's gelled SPE.

It is necessary to employ the advanced SPE, and the minimal packaging approach to achieve the energy density sought by LLNL. We believe that certain improvements in the SPE are achievable to produce the advanced SPE. These improvements include:

- Improving the cationic transport number to $t_+ > 0.9$
- Reducing the cell impedance to about 100 ohm cm^2
- Achieving a cathode capacity of 2.5 mAh/ cm^2
- Improving the lithium FOM to about 100 or more

The basic lithium-solid polymer electrolyte design includes thin layers of composite cathode (50 to 75 microns), of solid polymer electrolyte (typically 25 to 50 microns), and of a metallic lithium foil anode. This assembly, illustrated in Exhibit 5.1, is often referred to as a laminate.

In a practical cell, the laminate and cell dimensions are limited by processing considerations. The width and thickness are limited by the coating uniformity requirements. The length is limited by handling and packaging processes. The cell size and cell capacity are limited by the voltage/current and reliability requirements.

For a variety of reasons that are expanded upon below, a cylindrical cell design is recommended for this application, and offers flexibility for the assembly of a 60 kWh battery. The unit cell capacity in this concept would be about 300 Wh (75 Ah by about 4 volts). Seven cells would be arranged in a sub-assembly, each of which would provide 2.1 kWh. Thirty sub-assemblies would be brought together in each battery, to deliver a 63 kWh system.

Exhibit 5.1: The basic lithium-sold polymer electrolyte design includes thin layers of "composite" cathode (50 to 75 μm), of solid polymer electrolyte (25 to 50 μm), and of a metallic lithium foil anode. This assembly is called "laminate".

Within each cell, approximately 3.0 m^2 of active surface would be required. Cells would be about 9.3 cm in both length and diameter. The volume of each cell would be about 740 cm^3 , including packaging and metallic end caps. The sub-assembly volume would be 5.2 liters, or about 62% of the spar volume into which they would be loaded. The sub-assembly weight would be about 9.3 kg, providing about 225 Wh/kg. An illustration of the cell design is provided in Exhibit 5.2.

Accordingly to this concept, cylindrical cells would be mounted in the spar as sub-assemblies in a combination that would be compatible with the voltage/current requirements, charge control protocol, and would provide easy access for maintenance and replacement. An illustration of the sub-assembly concept is provided in Exhibit 5.3.

An analysis of cell design tradeoffs has been used to select optimal cell sizes. Exhibit 5.4 illustrates that specific energy greater than 200 Wh/kg could be achieved, without requiring cathode coating widths that are any greater than those which have been used and demonstrated to-date.

Exhibit 5.2: Cylindrical cell design (75 Ah) and cell assembly offers flexibility for the assembly of 60 kWh batteries in this concept, and limits parasitics.

Exhibit 5.3: Cylindrical cells can be mounted in the spar as sub-assemblies in a combination compatible with voltage/current, charge control protocol, and provide easy access for maintenance and replacement.

Exhibit 5.4: Analysis of cell design trade-offs indicates that specific energy greater than 200 Wh/kg could be achieved, without requiring cathode coating width greater than what has been demonstrated to-date.

In a sub-unit, the number of cells and their dimensions can be optimized to reduce the probability of a catastrophic mission interruption caused by failure of a unit cell or a sub-unit. Exhibit 5.5 illustrates the extent of system capacity associated with each cell as a function of cell length.

The attributes of an advanced SPE battery employing the minimal packaging concept would enable the production of a high specific energy density battery that would have the best prospects of meeting the requirements of the LLNL application. The engineering challenge of this approach would be minimized by a slight tradeoff of specific energy. Cell, sub-assembly and battery system are designed to maximize reliability. Furthermore, the minimal packaging concept provides a method to exceed the specific energy targets. It is quite possible that the only approach that would exceed the specific energy targets would require the use of the minimal packaging approach with the advanced SPE described above.

Exhibit 5.6 illustrates the gradual reduction of specific energy density for a given SPE technology, in this case the advanced SPE technology, using traditional packaging approaches. In contrast, Exhibit 5.7 illustrates the gradual reduction in specific energy when a minimal packaging concept is utilized. Thus, it is useful to recognize that even an advanced lithium-solid polymer electrolyte technology cannot meet the target specific energy density (180 Wh/kg versus more than 200 Wh/kg) when conventional battery packaging is used.

Exhibit 5.5: In a sub-unit, the number of cells and their dimensions can be optimized to reduce the probability of a catastrophic mission interruption caused by a unit cell and/or a sub-unit failure.

Exhibit 5.6: Battery system specific energy, based on an advanced LI-SPE configuration and conventional cell "packaging" could reach 180 Wh/kg.

Exhibit 5.7: Battery system specific energy, based on an advanced LI-SPE configuration and novel cell "packaging" could reach over 210 Wh/kg.

6.0 Thermal Management

For all battery systems considered in these analyses, some form of thermal management will be required, if only to control the thermal envelope in which the battery must operate. Since thermal management presents some form of a weight load and/or electrical load that reduces achievable energy densities, we have given brief consideration to the thermal management issue in this section.

For some systems, such as zinc-air and silver-zinc, a low round-trip efficiency imposes thermal management requirements. The requirements are actually for cooling during charge due to the heat generated during recharge. These systems prefer to operate at or near 25 degrees C in order to minimize capacity fade during cycling.

At the recharge rates employed in this application, heat generated during a recharge cycle is not typically due to iR in the battery. Energy released as heat during recharge will vary for each battery chemistry, and will depend on the thermodynamics associated with the specific battery chemistry. For the recharge rates of interest for this application, iR heating will probably be negligible.

In contrast, the high temperature systems considered in this study, namely sodium-sulfur, sodium-nickel chloride, and lithium aluminum-iron disulfide all operate at elevated temperatures in the range of 250 to 450 degrees C. These systems will not operate below certain thresholds. Furthermore cycle life and durability are severely impacted by higher temperature excursions.

Both the lithium-liquid electrolyte and the lithium-plasticized electrolyte systems operate best around 25 to 30 degrees C, though some variation upwards is easily tolerated. The lithium/PEO-based SPE systems operate best at temperatures between 50 and 80 degrees C.

For the application under consideration, the battery temperature can be increased using PV-generated power. The proposed PV design provides enough excess power to heat the battery. All the battery technologies considered have round-trip efficiencies much greater than 40%.

Initial thermal modeling for a Li/SPE battery system indicates that approximately 500 watts will be required to maintain the battery temperature at or above nominal operating temperatures. The battery temperature will be increased to about 40 to 45 degrees C at the end of charge (daytime period). The battery temperature will decrease to about 25 to 30 degrees C at the end of the discharge (night-time period). Very little radial and axial temperature gradients exist in the cell and/or sub-assembly.

7.0 Charge Rate

The effective charge period is reduced because of the decreased power of the PV during the early and last hours of sunlight. The situation is summarized in Exhibit 7.1. The battery system selected for the mission must be capable of accepting charge in less than 8 hours, without loss of capacity or decrease in cycle life. These are additional demands which will tend to eliminate some battery systems from consideration (e.g., silver-zinc).

Based on winter solstice (UT-Fig.5.3-1)

Exhibit 7.1: The effective charging period is reduced because of the decreased power of the PV during the early and last hours of sunlight.

8.0 Conclusions

This study has found that no battery technology presently available in commercial hardware can meet the specific energy demands and the cycle life requirements of the LLNL application. Prospects are somewhat better for some technology under development, although a novel packaging approach will be required to reduce parasitics.

For the more promising technologies, the following conclusions have been drawn:

- The zinc-oxygen has severe cycle life and capacity fade limitations
- The silver-zinc system comes close to achieving sufficient energy density at least to break the diurnal cycle. However, its charge rate limits its applicability.
- Lithium-titanium disulfide in a liquid electrolyte has shown good cycle life. However, its specific energy is too low (60 to 130 Wh/kg) for this application.
- Lithium-metal oxide in either liquid electrolyte or gelled SPE systems have either low specific energy or low cycle life.
- Lithium-solid polymer electrolyte systems in their present implementation, do not have adequate specific energy for this application.

A near-term objective of breaking the diurnal cycle can possibly be met by implementing a minimal packaging approach and optimizing system integration for an existing lithium-plasticized (gelled) electrolyte battery technology. Under such conditions, cycle life will still be limited relative to LLNL targets.

Finally, the LLNL performance requirements can best be addressed by pursuing a next generation, advanced solid polymer electrolyte battery technology, coupled with the minimal packaging concept described in this report. The SPE must utilize lithium metal anodes in order to achieve satisfactory specific energy. A development program dedicated to the specific mission requirements will be required to produce the desired test battery. Such a program may not be justified with the gelled SPE technology in that its prospects of achieving the longer term specific energy requirements of the LLNL application are not good. The implementation of a minimal packaging approach with this technology represents only an interim solution, at best.

The best opportunity to achieve, if not exceed the LLNL specific energy density requirements rests with the development of an advanced lithium-SPE technology which is implemented in a novel, minimal packaging approach. Such a battery system should provide more than 220 Wh/kg in fully packaged form.

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