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Electrochemical Systems with High Power Density: An Overview

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ADMINISTRATIVE INFORMATION

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1.0 INTRODUCTION

The design and fabrication process of a propulsion system for torpedoes and other undersea vehicles is a major undertaking. The selection of a power source for these vehicles from among those available is normally based on overall system requirements, and can be guided by a summary like the one presented in figure 1. Here, the power delivered, optimized for the weight of the energy converter, is plotted against the mission duration. In the propulsion of torpedoes, which require high power densities for a short period of time, electrochemical power sources are in competition with thermochemical sources. Each system has its problems and desirable features, and both approaches have been used, or are being developed, to propel torpedoes. For instance, the British, French, Italian, and Soviet Navies have developed electric propulsion in their torpedoes. The U.S. Navy is currently developing a stored chemical energy propulsion system (SCEPS) in the Mk 50 torpedo. Tables 1 and 2 compare high-energy thermal and electrical propulsion systems. From these tables, it can be seen that the energy densities of advanced thermal and electrical propulsion systems are projected to be approximately equal (Szpak and Driscoli, 1987). The scope of this discussion, however, is not to compare the two propulsion technologies, but to provide an overview of electrochemical systems with high power density. The existence of other propulsion technologies is simply pointed out for the sake of completeness.

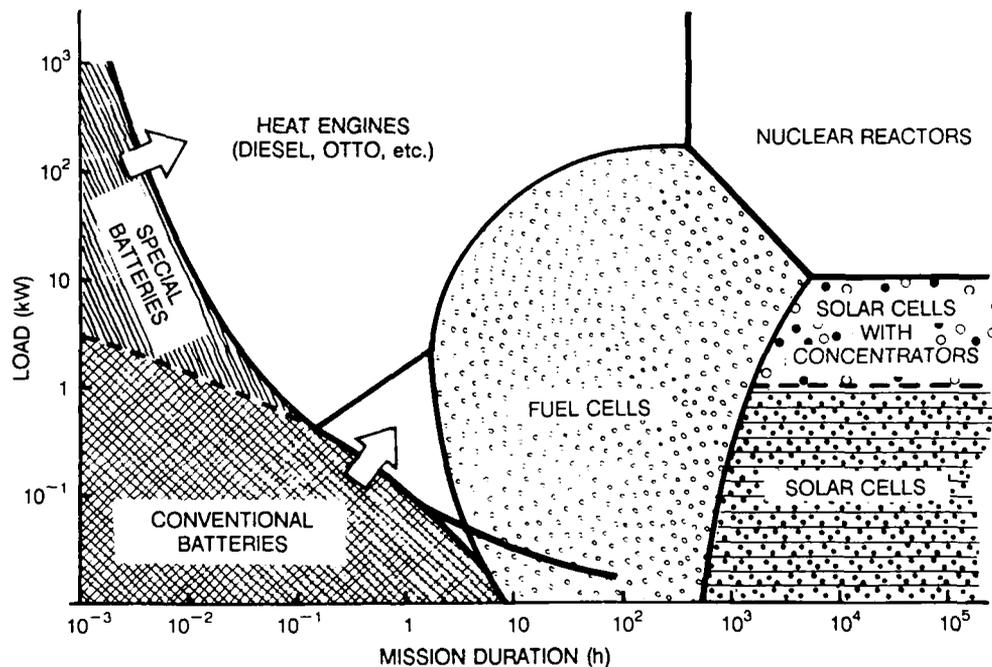


Figure 1. Power versus mission duration—regions of applicability of various energy converters, optimized for weight.

Table 1. Comparison of various propulsion systems.

Characteristic	System				
	Li/SF ₆	ADSCEPS	Li/AgO	Al/AgO	Li/SOCl ₂
Theoretical specific energy (Wh/kg of reactant)	3600	3600	1370	1040	1470
Conversion efficiency	0.21	0.27	0.41	0.44	0.77
Utilization	0.88	0.9	0.7	0.7	0.6
Practical specific energy (Wh/kg of reactant)	665	875	390	320	680 *

*NOTE: A practical specific energy of 880 Wh/kg of reactant appears possible with silicon incorporated into the cathode.

Table 2. Energy densities of selected propulsion systems.

Characteristic	System		
	SCEPS	ADSCEPS	Li Batteries *
Specific energy (Wh/kg)	97	130	100
Specific energy (relative to SCEPS)	1.00	1.34	1.03
Energy density (Wh/l)	144	190	190
Energy density (relative to SCEPS)	1.00	1.32	1.32

*NOTE: Projections are about the same for Li/AgO, Al/AgO, and Li/SOCl₂ battery systems.

Suppose it has been decided, from the overall requirements, that electric propulsion is the preferred choice to power a hypothetical undersea vehicle. Prior to selecting a suitable battery system, a number of questions must be considered.

1. What are the energy and endurance requirements for the proposed vehicle? What is the time duration of the mission?
2. Is the mission one-time-only, as for a torpedo? If so, primary batteries can be used. If the vehicle will undergo a number of missions, a secondary, rechargeable battery is the preferred choice.
3. Does the mission of this vehicle require that the energy converter be able to provide different power levels? If it does, the requirement adds further constraints in choosing a suitable battery system to drive the vehicle.
4. How much space in the proposed vehicle is allotted for the propulsion system? What is the geometry of that space? Where is the location of the propulsion system in the vehicle? In torpedo design, the propulsion system is designed first. However, this is usually not the case if the battery is going to be used to provide power to an unmanned submarine or other undersea vehicle.
5. How will the battery be activated?
6. What are the safety considerations?

Depending on the battery system under consideration, there are other questions that need to be addressed, such as operational temperature, thermal management, and corrosion. The following discussion will be general in nature. Battery characteristics will be discussed and their importance in selecting an appropriate system will be illustrated. Many battery systems are available, and it is beyond the range of this report to discuss them all. Since a high-energy system is required to drive an undersea vehicle, only systems with high power density will be considered. Note that, in choosing and developing a propulsion system, extensive research (i.e., computer modeling and electrochemical experiments) will be required.

2.0 BATTERY CHARACTERISTICS

2.1 DEFINITION OF A BATTERY

Devices that convert chemical energy into electrical energy are commonly referred to as batteries. In these devices, high-energy chemical compounds are converted to other chemical compounds that have lower energy content. In the conversion process, electrical energy is produced. The simplest battery consists of a single cell. Figure 2 illustrates the functional elements present in a Li/SOCl₂ battery. Other batteries have the same functional elements (Tiedeman et al., 1978). Typically, a cell consists of an electrode that acts as a source of electrons (an anode), a porous nonconductive separator, and an electron sink (a cathode). The final basic cell component is the electrolyte, which is an aqueous or non-aqueous solution of an ionizable salt. The operation of a battery is a dynamic process, consisting of a series of elementary processes in which the slowest one determines the rate. These processes are: (1) transport of participating species (reactants) toward the electrode surface; (2) adsorption on the electrode surface; (3) charge transfer; (4) desorption of reaction products; (5) transport of reaction products away from the electrode surface; (6) ion conduction through an electrolyte; and, to complete the cycle, (7) flow of electrons in an

external circuit where the electrical work is delivered. These processes, together with the respective driving forces, are shown in figure 3. Each battery system has its own inherent properties such as specific energy, specific power, and system utilization. These properties aid one in selecting a suitable system to power a particular vehicle (Mosier-Boss et al., 1987).

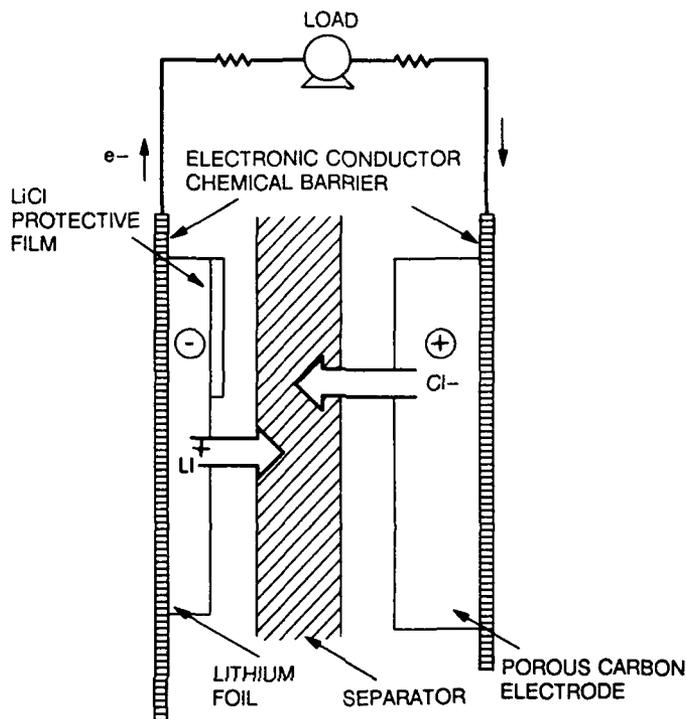


Figure 2. Cross section of the Li/SOCl₂ cell.

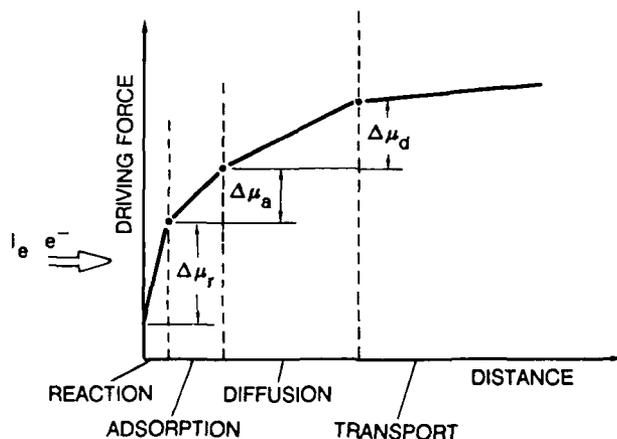


Figure 3. Fluxes and associated driving forces operating during cell discharge. I_e is the electronic current; $\Delta\mu$ is the driving force expressed in volts. Subscripts denote the fluxes; r = charge transfer reaction, a = adsorption, and d = diffusion.

2.2 SPECIFIC ENERGY AND SPECIFIC POWER

One cannot discuss specific energy without also discussing specific power. Figure 4 shows the typical relationship between specific energy and specific power available from a battery. Specific power (W/kg) or power density (W/dm^3) is proportional to the rate of discharge, whereas specific energy (Wh/kg) or energy density (Wh/dm^3) of a given system is proportional to the amount of stored energy per unit weight or unit volume of material. Therefore, the plot in figure 4 indicates that the rate of discharge (i.e., specific power) increases as the amount of stored energy (i.e., specific energy) decreases.

Specific energy is determined by the working cell voltage, equivalent weight, and mass density of the system. Plots of theoretical specific energy as a function of equivalent weight, equivalent volume, and cell voltage for a number of electrochemical systems is shown in figure 5. This figure clearly illustrates that higher cell voltage, lower equivalent weight, and higher equivalent mass density lead to relative increases in the energy content of a given system. The advantages of higher energy become obvious when the ultimate use of the battery is sensitive to weight, volume, and number of cells.

While specific energy can be used to assess the maximum potential of a system, knowledge of the specific power or power density capabilities determine energy availability as a function of discharge rate. Figure 6 gives a comparison of specific power as a function of specific energy for several systems. A highly efficient system is characterized by a vertical line.

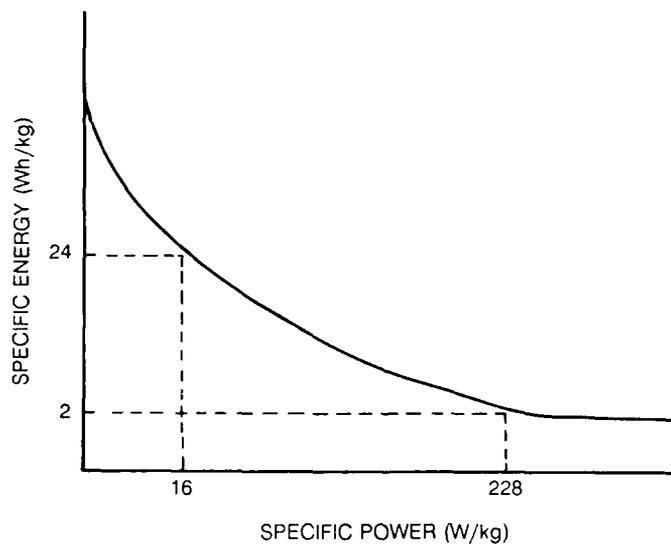


Figure 4. Specific energy as related to specific power.

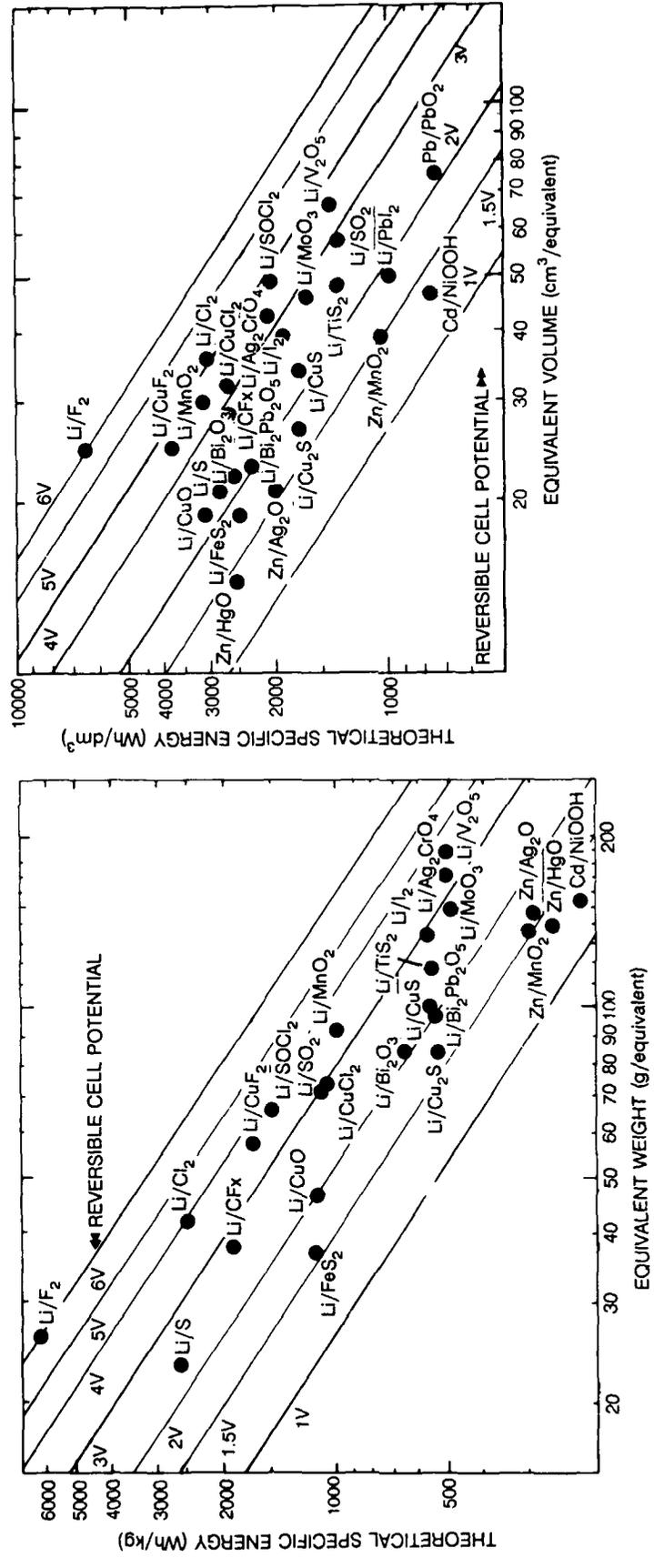


Figure 5. Plots of theoretical specific energy as a function of equivalent weight, equivalent volume, and cell potential.

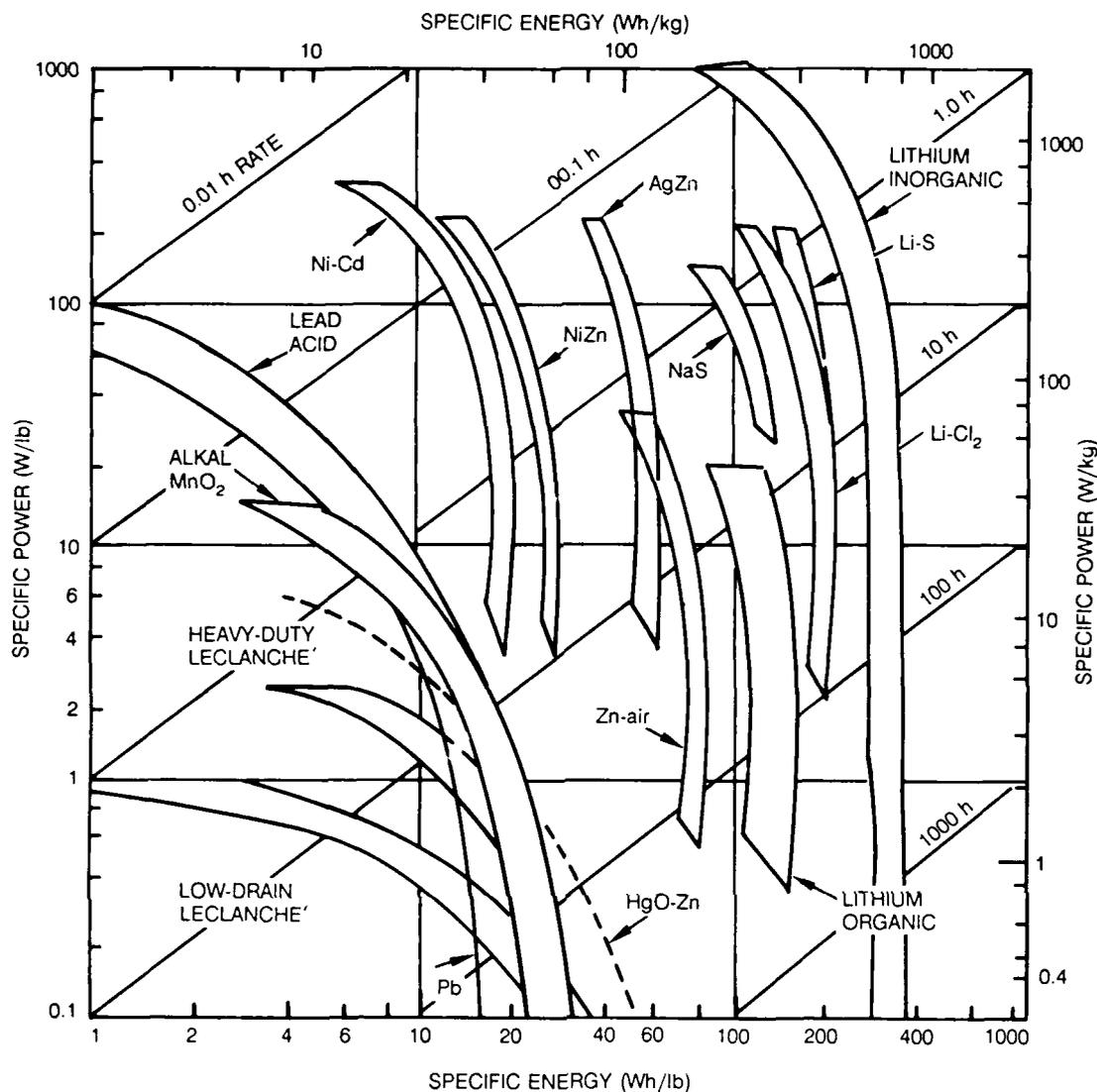


Figure 6. Performance capabilities of various batteries.

2.3. SYSTEM EFFICIENCY

2.3.1. Engineering Efficiency

The performance of a given system can be assessed by its coulombic, energy, material utilization, voltaic, and thermal efficiencies. Coulombic efficiency is a measure of the reversibility of electrode processes and is, for a specific set of conditions, the number of coulombs obtained during discharge over those returned on charge. Significant deviations from 100% coulomb efficiency suggest the growing importance of parasitic side reactions. A decrease in efficiency can result from any one, or combination, of the following: (1) electrochemical decomposition of the electrolytic solution; or (2) corrosion of the electrode or electronic support matrix. Significant reduction in coulombic efficiency can be seen at both high and low temperatures, high charging voltages, and high contamination levels.

Energy efficiency is determined by multiplying the coulombic efficiency by the ratio of the average discharge cell voltage to the average charge voltage. It is typical to have a coulombic efficiency of 98% and an energy efficiency of only 50%. This difference is related to negative effects of electrode polarization, electronic and ionic resistances, and mass transport limitations on the observed system voltage. The relative importance of these effects is specific to a given system and application.

Material utilization efficiency, or faradaic efficiency, is defined as the ratio of the material used in the production of electricity to that supplied to the cell under a given set of conditions. Factors tending to reduce material utilization efficiency are (1) coverage of the active surface by insoluble reaction products; (2) mass transport limitations; (3) electronic isolation of active materials; (4) imposed voltage shutoff; (5) significant self-discharge processes; (6) significant changes in material morphology; (7) solubility of reactants and products; and (8) contamination of active materials.

2.3.2. Thermodynamic Efficiency

The voltaic efficiency is the ratio of the working cell potential to the reversible cell potential. Thus it is unity when current is zero. When current is drawn from an electrolytic cell, the cell potential, as well as the voltaic efficiency, drop because of irreversible processes occurring in the cell. To maximize the useful energy delivered by the cell, these losses must be minimized. Potential losses, often called overpotential, can be attributed to three causes; surface overpotential, resistance overpotential or ohmic losses, and concentration overpotential.

Thermal efficiency is the ratio of the Gibb's free energy, ΔG , to the Helmholtz free enthalpy, ΔH . Not much can be done to increase thermal efficiency as it is fixed by the selection of an electrochemical couple.

For practical purposes, an additional efficiency is usually specified—the engineering efficiency. It includes all the efficiencies associated with the construction materials, cell design, parasitic reactions, etc. The parasitic reactions are those that do not contribute to the production of electric power. On the contrary, they may cause the failure of the device, often a catastrophic failure. It is here that scale-up problems emerge. Except for thermal efficiency, all these efficiencies depend on the design of the battery.

Figure 5 shows plots of theoretical specific energies as a function of equivalent weight, equivalent volume, and cell voltage. As mentioned earlier, a high-energy system is required in the propulsion of an undersea vehicle. Therefore, only systems with specific energies greater than 400 Wh/kg will be discussed. Additional systems not shown in figure 5, but which will be discussed, are presented in table 3. These systems fall into one of the following categories: molten-salt batteries (e.g., Li/S and Li/FeS₂); solid-electrolyte batteries (e.g., Na/S); high-energy, reserve, flowing batteries (e.g., Zn/Cl₂, Al/AgO, Li/AgO, and Zn/Ag₂O₂); and high-energy, reserve, static electrolyte batteries (e.g., Li/SOCl₂ and Li/SO₂Cl₂). In the ensuing discussion, advantages and disadvantages of these battery systems will be pointed out.

Table 3. Additional high-energy systems under consideration.

System	Theoretical Specific Energy (Wh/kg)	Cell Potential (V)	Maximum Current Density (mA/cm ²)
Li/AgO	1370	3.52	-
Al/AgO	1040	1.4 - 1.6 ^a	1000
Li/SOCl ₂	1470	3.66	100
Li/SO ₂ Cl ₂	1404 ^b	3.90	-
Mg/AgCl	450	1.2	350
Zn/AgO	540	1.4	250

^a A range of cell potentials exists because of the presence of aluminum oxides in the anode.

^b Calculated from the cell potential.

3.0 THERMAL BATTERIES

3.1 USES OF THERMAL BATTERIES

Thermal batteries of high specific energy and high specific power are being developed for two major applications: (1) electric-powered automobiles, and (2) load-leveling, energy-storage devices for electric utility systems (Battles, 1976). In the case of electric-powered automobiles, the emphasis is on designing a high-energy battery that will not occupy much space in the vehicle nor appreciably add weight to the vehicle. Chloride Silent Power Limited (CSPL)¹ is currently developing a Na/S battery to power the Bedford CF van, developed by Lucas Chloride EV Systems Limited² and General Motors³ (Bindin, 1986). Energy storage devices commonly use the LiAl/FeS_x battery (Bennion et al., 1988). These energy-storage devices are very large and are designed to rest on the bed of a trailer truck. For these applications, the batteries are designed to be rechargeable. However, thermal batteries can also be designed to be used as primary batteries, as they are in many military applications. Depending on the electrolyte used, thermal batteries are often subdivided into two groups—molten-salt batteries and solid-electrolyte batteries.

3.2. MOLTEN-SALT BATTERIES

3.2.1. Specific Power and Specific Energy

A specific power and specific energy diagram for conventional and advanced systems is shown in figure 7. A grid of the projected ranges of a 1300-kg automobile with a 300-kg battery at different speeds is drawn in. This grid is comparable to an undersea vehicle requiring different power levels. As the vehicle changes power levels, we do not want to sacrifice either specific power or specific energy. To maximize both the specific power and

¹ Daven Rd., Astmoor, Duncorn, Cheshire, England.

² Solihull, W. Midlands, England.

³ Detroit, MI.

energy, we must find a system that minimizes the curvature observed in the plots of specific power versus specific energy. From figure 7, systems that exhibit greatly minimized curvatures in their specific power versus specific energy plots are predominantly molten-salt batteries. This, in part, results because of the high conductivities of the molten-salt electrolyte (Attewell and Clark, 1981; Interagency Advanced Power Group, 1989).

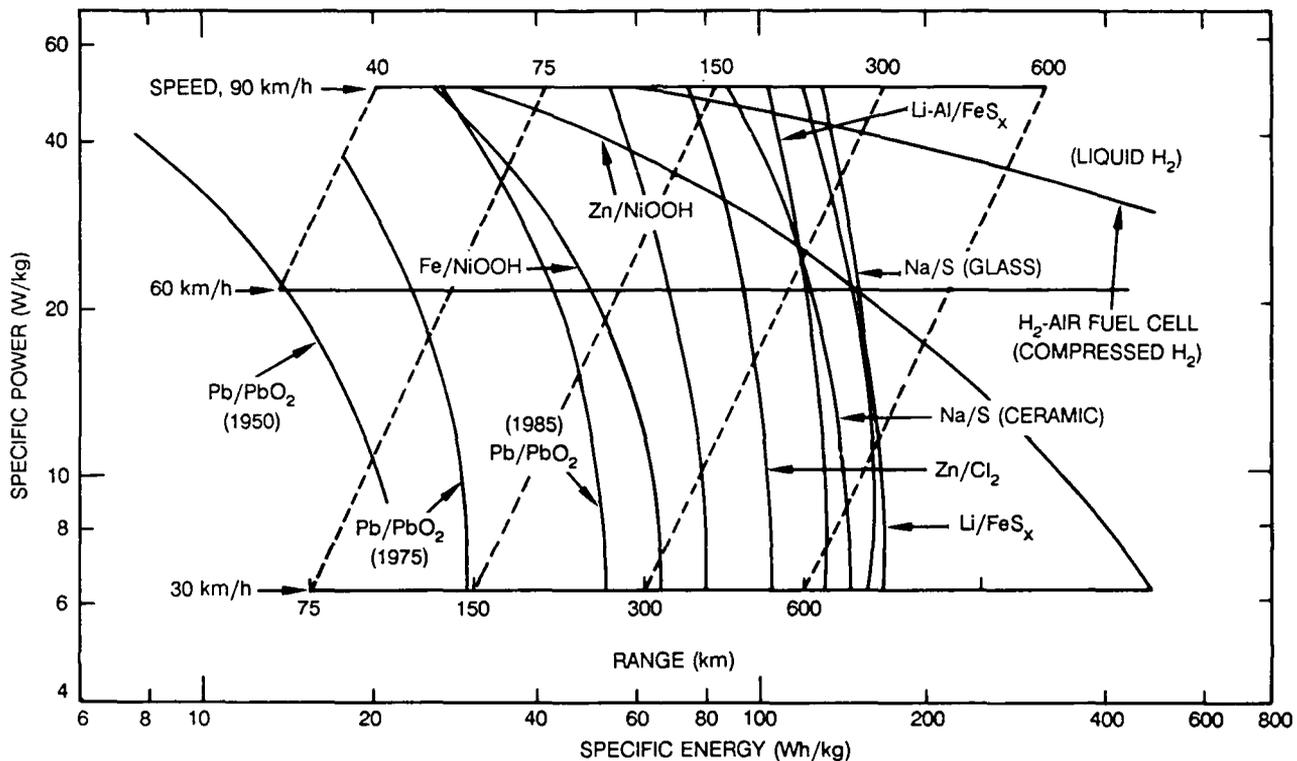


Figure 7. Specific power and specific energy diagram for various battery systems. Grids represent different speeds of a 1300-kg automobile.

3.2.2. Inorganic Molten-Salts

3.2.2.1. Properties

The commercially available molten-salt systems use inorganic electrolytes⁴. The most common electrolyte is a eutectic mixture of lithium and potassium chlorides with a melting point of 352°C. Its high decomposition potential allows the use of alkali and alkaline earth metals as anodes. Until recently, calcium and magnesium were the only metals employed, but now lithium, either as the pure metal or alloyed with Al, Si, or B, is coming into use. At a working temperature between 400°C and 600°C, this electrolyte is almost fully ionized, requires no solute, and has a conductance of 1.85 ohm⁻¹cm⁻¹ (by comparison, a 1-M aqueous solution of NaCl has a conductance of 0.0778 ohm⁻¹cm⁻¹ at 20°C,

⁴Note that developmental work on room temperature molten-salts (i.e., LiCl-AlCl₃-imidazolium chloride and LiCl-AlCl₃-n-butyl pyridinium chloride) is currently being performed by J. Wilkes, (719) 472-2655, Department of Chemistry, Air Force Academy, Colorado Springs, CO.

while a 5.3-M solution has a conductance of $0.225 \text{ ohm}^{-1} \text{ cm}^{-1}$) and a viscosity of 1.9 centipoise (cP) compared with water, which has a viscosity of 0.89 cP at 20°C and 1.002 cP at 25°C . Combined with suitable cathodes that may be very soluble (dichromates), soluble (chromates), or insoluble (sulfides), cell potentials near 3 volts are available. Cells constructed from these materials can be discharged at current densities up to several amperes/ cm^2 . In combination, these properties allow molten-salt batteries to be constructed so that, at very high discharge rates, they give power densities that are superior to any other class of battery.

Molten-salt batteries using inorganic electrolytes must be operated at greatly elevated temperatures to melt the electrolyte. Hot, molten electrolytes are very corrosive. Normally, the battery must be built from materials that are corrosion resistant to molten alkali halides and dissolved metal sulfides at temperatures on the order of 300 to 600°C . However, if the mission of the vehicle is of a short duration, this is not a major consideration. Since no gaseous products are theoretically formed, there is no need for phase separators or vents.

3.2.2.2. Storage and Activation

The fact that the electrolyte is solid at room temperature presents no problem in terms of shelf life and safety. Under normal storage conditions, a properly constructed battery has an almost indefinite shelf life. However, these batteries must be activated by melting the electrolyte. There are two ways of doing this. One way is to have the electrolyte in a reservoir. Using a heating device, the electrolyte is melted and pumped into the cells. The problem with this method is achieving uniform distribution of electrolyte quickly into all cells of the module. The second approach, which is used in the energy storage devices and the Na/S battery-powered automobile, is to prepare a bipolar stack of cells with solid electrolyte already incorporated in the cells. In this method, there will be a uniform distribution of electrolyte. As discussed earlier, a cell is composed of an anode, cathode, electrolyte, and separator. A bipolar stack of cells is simply a stack of cells connected in series. The batteries used in energy storage devices are very large and are made up of numerous modules containing the bipolar stack of cells. Although much smaller, the Na/S battery being designed by CSPL to power the CF Bedford van will also be made up of modules containing bipolar stacks of cells. These modules are interconnected by a busbar and are surrounded by heaters used to melt the electrolyte in the cells. The heaters also serve a second purpose—to keep the modules of the battery at their operating temperatures. The batteries used for these applications are designed for long lifetimes and are rechargeable. Consequently, during long operating times and during the discharge-recharge cycling, the battery must be maintained at elevated temperatures. A bipolar stack approach to cell design may, in order to achieve homogeneous melting of the electrolyte, limit the size of the cells. In fact, construction of large batteries composed of cells having outer diameters greater than 3.0 inches has not been achieved because of thermal runaway. This results in expansion of the battery, which in turn results in breaching of the battery structure followed by leakage of the hot, molten battery contents. In the power-dense battery systems under consideration for propelling a vehicle, the anode consists of either metallic lithium or lithium alloys, and molten lithium is very reactive, especially in the presence of water.

3.2.2.3 Military Applications

The primary use of molten-salt or thermal batteries in military vehicles has been to provide power to the electronics, pumps, valves, etc., of that vehicle. For these uses, the batteries are small. The Mk 50 torpedo uses a Li/FeS₂ thermal battery to power the

torpedo while the boiler is being activated. This particular battery consists of 80 cells, and is 2 inches in diameter and 4 inches in length. The design of these batteries must be such that, following storage, the electrolyte can be melted and power generated very quickly. Figure 8 shows the internal construction of a typical thermal battery used to power the electronics of military vehicles. Activation time is defined as the period from starting the ignition of an internal pyrotechnic charge to the appearance of useful electrical output, and can vary from 50 ms to several seconds depending on the size of the battery, its construction, and its electrochemical system. These batteries are activated by a squib, which ignites a pyrotechnic present in the bipolar stack. In the case of the Mk 50 thermal battery, the pyrotechnic is Fe-KClO₄. This pyrotechnic melts the electrolyte used in the molten-salt battery and gets the battery up to its operational temperature. The battery remains active for as long as 1 hour, or for only a few seconds, depending on its size, thermal insulation, electrochemical system, the ambient temperature, and the rate at which power is withdrawn. Obviously, a battery that uses a pyrotechnic to activate it is not going to be rechargeable. According to NSWC, there is one potential problem with using squibs to activate these batteries on naval ships. The batteries can be unintentionally activated simply by turning on the ship's radar.

3.2.2.4. Molten-Salt Redox Couples

Some candidate molten-salt systems for driving a hypothetical undersea vehicle are tabulated in table 4. Of these, the Li/S system has the highest cell potential and theoretical specific energy. Its maximum operating temperature is below 440°C, the temperature at which S melts. The Li/S system does, however, have two inherent problems. First, the cathode collector contains elemental sulfur. Consequently, it must be made of a corrosion-resistant material. Typically, C and Mo are used. Second, during the course of discharge, Li polysulfides are formed that are soluble in the melt. Both of these problems shorten the lifetime of the battery. However, if the mission of the vehicle is on the order of 2 to 4 minutes, these inherent problems of the Li/S system should pose no difficulties.

Batteries using the Li/FeS system have currently been fabricated and tested with power densities approaching 1000 W/kg. Current work at the Naval Surface Weapons Center, (NSWC) White Oak, MD [Dr. S. Dalek (202) 394-1364] projects power densities in excess of 1 kW/kg. Construction of large batteries, (i.e., having an outer diameter greater than 3 inches) has been unsuccessful thus far because of thermal runaway followed by the usual catastrophic consequences. The initiation of thermal runaway is attributed to thermal decomposition of FeS followed by a highly exothermic reaction between the gaseous sulfur and molten lithium. The Li/FeS_x systems have a very complicated discharge path owing to the existence of stable intermediates. Note that the purpose of alloying Li with B, Al, and Si in the FeS and FeS₂ cells is to improve discharge performance and to immobilize or contain the molten lithium (at 500°C, molten lithium has a density of 0.5g/ml and a viscosity of 3.5 mP). However, in these cells additional weight is added by the Si, B, and Al since these species do not take part in the electrochemical reaction. Furthermore, the Li alloys with B, Al, and Si are less reactive than pure Li. Two US organizations are currently engaged in developmental work on Li/FeS_x molten-salt batteries: SAFT of America⁵ and Catalyst Research.⁶ Developmental work is also being carried out at the US Army Harry Diamond Laboratory, Washington, DC [contact: Walt Cooper, (202) 394-3114].

⁵ 107 Beaver Court, Cockeysville, MD 21030.

⁶ Catalyst Research Corp., 1421 Clarkview Rd., Baltimore, MD 21209.

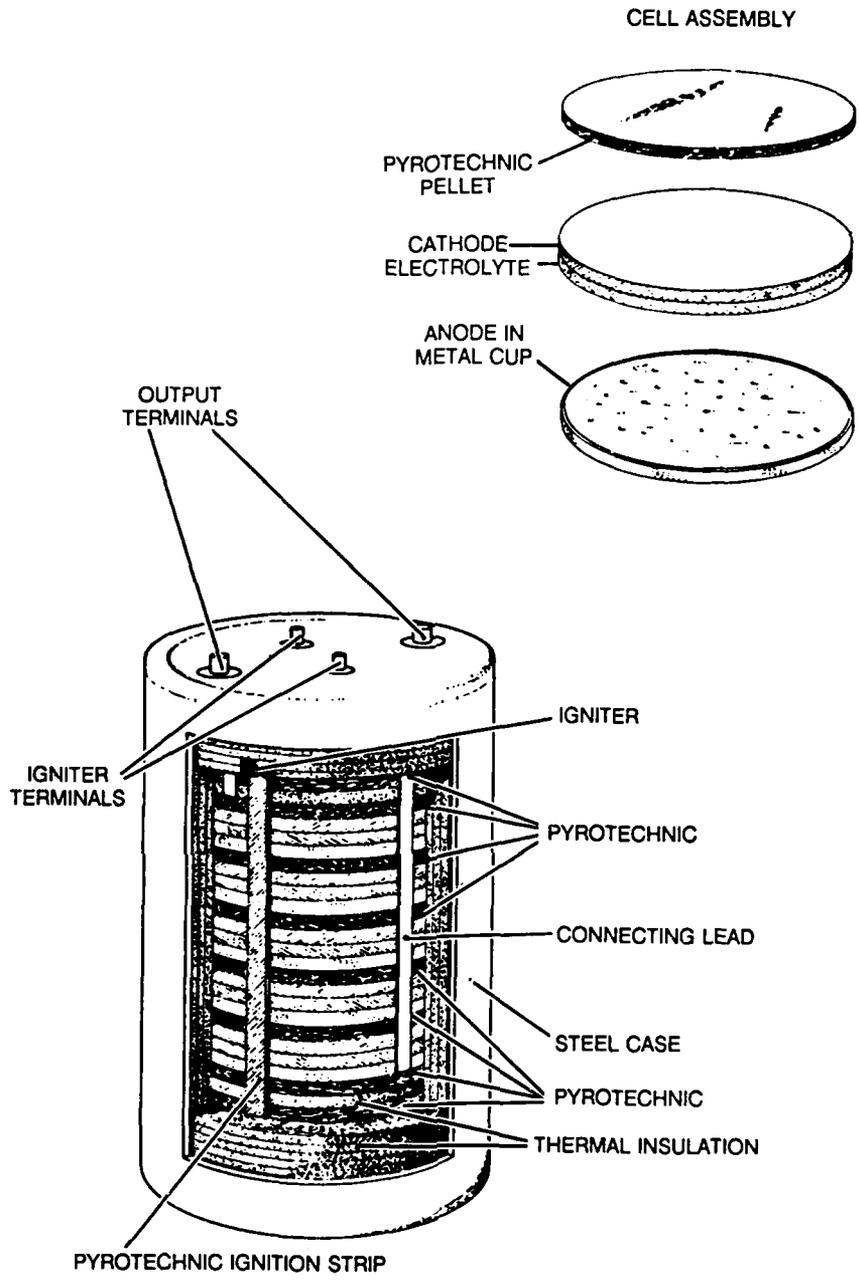


Figure 8. Internal construction of a typical thermal battery.

Table 4. Properties of some inorganic molten-salt systems.

Molten-Salt System	Overall Reaction	Electrolyte	Operating Temperature (°C)	Cell Potential (V)	Theoretical Specific Energy (Wh/kg)
Li/S	$2\text{Li} + \text{S} \rightarrow \text{Li}_2\text{S}$	LiCl-KCl	400	2.23	2600
LiAl/FeS	$2\text{LiAl} + \text{FeS} \rightarrow \text{Li}_2\text{S} + \text{Fe} + 2\text{Al}$	LiCl-KCl	450	1.33	458
Li ₄ Si/FeS ₂	$\text{Li}_4\text{Si} + \text{FeS}_2 \rightarrow 2\text{Li}_2\text{S} + \text{Fe} + \text{Si}$	LiCl-KCl	450	1.8, 1.3	944
Li ₄ Si/FeS ₂	$\frac{1}{2}\text{Li}_4\text{Si} + \text{FeS}_2 \rightarrow \text{Li}_2\text{FeS}_2 + \frac{1}{2}\text{Si}$	LiCl-LiBr-KBr	400	1.8	652
LiAl/FeS ₂	$2\text{LiAl} + \text{FeS}_2 \rightarrow \text{Li}_2\text{FeS}_2 + 2\text{Al}$	LiCl-LiBr-KBr	400	1.8	514
Li/FeS ₂	$\text{FeS}_2 + 4\text{Li} \rightarrow 2\text{Li}_2\text{S} + \text{Fe}$	LiCl-KCl	430	1.75	1273

3.2.3. Organic Molten Salts

Although room-temperature molten-salt batteries are not yet commercially available, research going on at the Air Force Academy looks very promising. Table 5 tabulates theoretical specific energies and cell voltages for systems currently under investigation. According to J. Wilkes of the Air Force Academy, the proposed maximum operating temperature of these batteries will be 100°C. At this temperature, the viscosity of the electrolyte is reduced, thus increasing electrolyte conductivity and thereby facilitating mass transport within the cells. At temperatures higher than 100°C, decomposition of the imidazolium ring occurs. Research plans include the construction and discharge of prototype cells.

Table 5. Some proposed room-temperature molten-salt batteries. The electrolyte is 33 mole % ImAlCl₄ buffered with either NaAlCl₄ or LiAlCl₄.

Electrode Couple	E (V)	Theoretical Specific Energy (Wh/kg)
Li/Cu	2.761	776.3
Li/Ag	2.847	506.4
Na/Cu	2.757	600.9
Na/Ag	2.843	458.2

3.3. SOLID-ELECTROLYTE BATTERIES

3.3.1 Properties

Solid-electrolyte cells include the Na/S cells, in which the electrolyte is a glass or ceramic that conducts only sodium ions (Bennion et al., 1988). As shown in figure 7, the plot of specific power versus specific energy exhibits minimum curvature, which, as discussed earlier, is a desirable feature. In addition, these cells have reasonable cell voltages and high theoretical specific energies, as shown in table 6. A great deal of what was discussed about molten-salt cells applies here as well. Although corrosion is a problem with these cells during continuous use, it would pose no difficulties for a vehicle whose mission is on the order of a few minutes.

Table 6. Properties of some solid-electrolyte systems.

Solid-Electrolyte Cell	Overall Reaction	Operating Temperature (°C)	Cell Potential (V)	Theoretical Specific Energy (Wh/kg)
Na/Na+Solid/S ^a	$2\text{Na}+3\text{S}\rightarrow\text{Na}_2\text{S}_3$	350	2.08-1.7	758
Na/Na ₂ O·XAl ₂ O ₃ /SCl ₃ AlCl ₄ in AlCl ₃ -NaCl ^b	$4\text{Na}+\text{SCl}_3\text{AlCl}_4+3\text{AlCl}_3\rightarrow 4\text{NaCl}-\text{AlCl}_3+\text{S}$	250	4.2	563
Na/Na ₂ O·11Al ₂ O ₃ /NaAlCl ₄ /FeCl ₂	$2\text{Na}+\text{FeCl}_2\rightarrow 2\text{NaCl}+\text{Fe}$	250	2.35	774

^a Solid is either a glass or a ceramic, Na₂O·9Al₂O₃/S.

^b Lab cell only.

The Na/S system is rechargeable and exhibits a 100% Coulombic efficiency; i.e., no measurable self-discharge is observed in Na/S cells during prolonged periods at open circuit. Consequently, the major developmental area has been in secondary batteries. However, difficulties in cell design and fabrication have been encountered. Because of the thermal and mechanical stresses experienced during their discharging/charging cycles, these cells tend to crack and break. However, if the mission of the vehicle is one-time-only for a short duration, this is not a consideration. As with the molten-salt modules, the solid-electrolyte cells also must be small to prevent thermal runaway. The cells produced by CSPL to be used in the Bedford CF van are 4 cm in diameter, 4 cm in length, and are approximately 100 g in weight.

3.3.2. Current Developmental Research

Note that developmental research on Na/Na₂O·9Al₂O₃/organosulfur cells is underway (additional information can be obtained from Elton Cairns, Lawrence Berkeley Laboratory, University of California, Berkeley). These new cells have some very attractive features: (1) low temperature of operation (about 100°C); (2) noncorrosive; (3) reasonable energy densities (350 to 700 Wh/kg, depending on the organosulfur compound used); and (4) easy to manufacture.

Developmental research on Li/solid state/polymer cells is also underway (additional information can be obtained from Dale Shockler, Mead Corp.⁷) The cells are typically 4 to 12 mils thick. The achieved energy and power densities are 200 Wh/kg and 650 W/kg. The open-circuit cell voltage is 3.0 V and the maximum discharge current density is 50 mA cm⁻². These cells are rechargeable and the maximum number of cycles so far achieved is 1000.

3.4 TECHNOLOGY ISSUES

Thermal batteries have some very desirable features. However, there are obviously questions that must be addressed concerning the potential use of thermal batteries to power an undersea vehicle. These include:

1. Thermal batteries with cell outer diameters greater than 3 inches have not yet been achieved because of problems with thermal runaway. Can these scale-up problems be solved?
2. If the scale-up problems are solvable, how is such a large battery going to be activated, and how much time will be required to activate a large thermal battery?
3. It is common for small thermal batteries to be activated by using a squib and a pyrotechnic. Caution is required, however, because it is possible for some squibs to be activated by simply turning on the ship's radar. Is this going to be a problem for the power source of the vehicle? What are the safety considerations should a large thermal battery become accidentally activated?
4. Thermal batteries operate at elevated temperatures. What is the highest skin temperature that can be tolerated? Are these elevated temperatures going to affect the electronics of the vehicle?

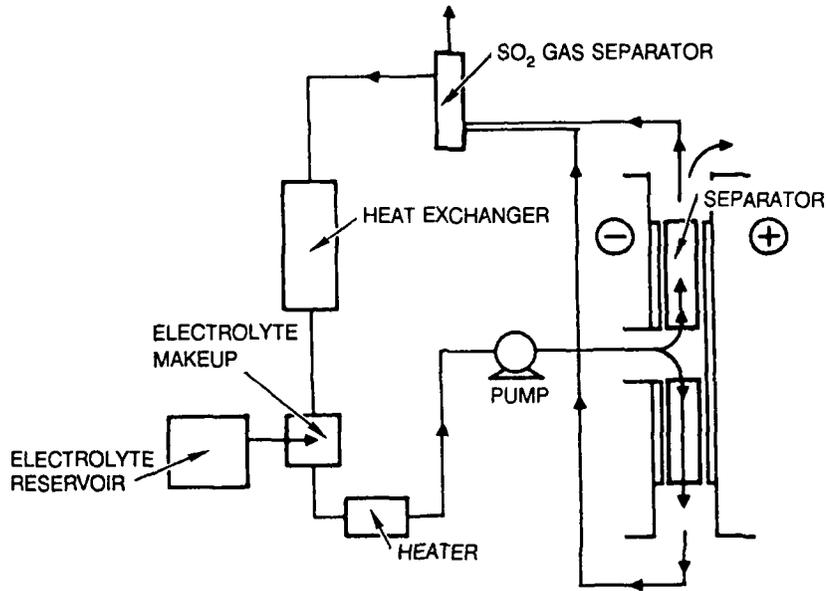
⁷ Courthouse Plaza, Dayton OH 45463.

5. At these elevated temperatures, the electrolyte is molten, as is the lithium anode. Even when not discharging, at these elevated temperatures the material of the battery is molten. This is potentially dangerous. Should it become necessary to recover the vehicle, what would be the shutoff procedure of the battery, and is it safe?

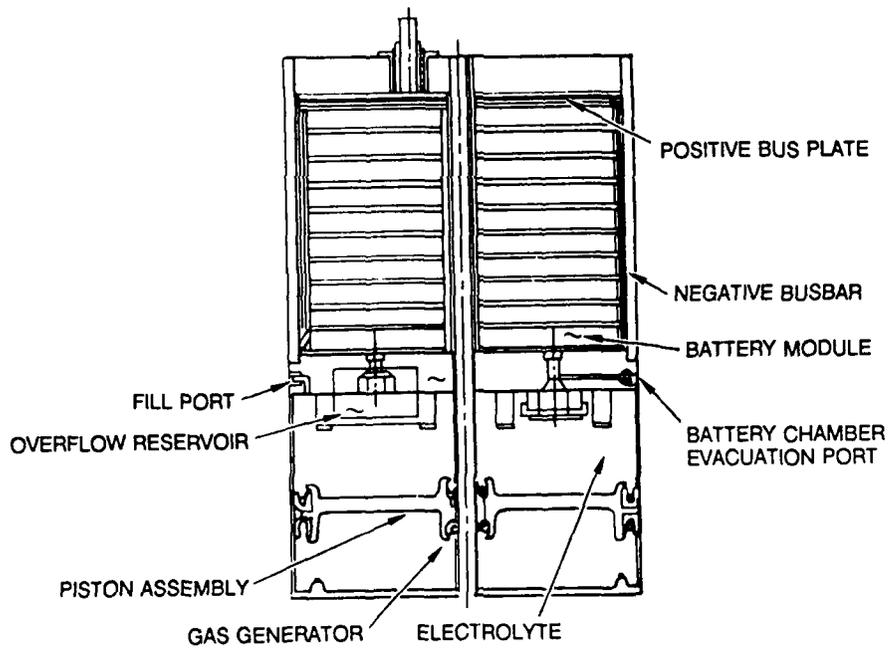
4.0 HIGH-ENERGY RESERVE BATTERIES- FLOWING AND STATIC ELECTROLYTE

4.1. FLOWING ELECTROLYTE VERSUS STATIC ELECTROLYTE

From table 3 and figure 5, it can be seen that a large number of battery systems with high cell voltages and theoretical specific energies use electrolytes that are liquid at room temperature. A reserve, or reservoir, must be used in the high-energy systems to separate the electrolyte from the electrodes, since these systems spontaneously discharge once the circuit is completed. To activate the system, either a flowing electrolyte or a stationary electrolyte is employed. Figure 9 illustrates both of these concepts in the Li/SOCl₂ system. The battery that uses a flowing electrolyte is much more complicated than one using a static electrolyte. The design of a reserve battery employing a stationary electrolyte, shown in figure 9, consists of three subsystems: a battery module, an electrolyte reservoir, and a mechanism to force stored electrolyte into the battery module. The principal advantages of this approach, therefore, are the simplicity of the design and the compactness of the device. Because of the larger number of components in the flowing electrolyte system, one would expect the static electrolyte system to be more reliable. However, there are advantages, as well as disadvantages, to the flowing electrolyte system and these are tabulated in table 7 (Mosier-Boss et al., 1987; Bennion et al., 1988; West et al., 1986; Szpak and Venkatasetty, 1983; Kilroy et al., 1987; Momyer and Littauer, 1982).



(a)



(b)

Figure 9. Battery designs proposed for the Li/SOCl_2 system. (a) Flowing electrolyte system. (b) Static electrolyte system.

Table 7. Advantages and disadvantages of flowing electrolyte systems.

ADVANTAGES:

1. Oxidant, reductant, and/or product go in or out of the electrode stack.
2. Heat is easily transported in or out of electrode stack.
3. Side products removed from stack.
4. Impurities can be removed from circulating electrolytic solution.
5. External storage may allow approach to theoretical specific energy.
6. External storage of oxidant and reductant allows for greater safety with highly energetic systems.
7. Greater control of the operating conditions.

DISADVANTAGES:

1. Complex piping and pumping design problems.
2. Packaging difficult, especially small sizes.
3. Maintenance problems.
4. Engineering development costs high.
5. Electrode and flow geometry critical.

4.2 SEAWATER BATTERIES

Despite their complexity, flowing electrolyte systems have been and are still being used in the propulsion of undersea vehicles. The systems in which flowing electrolytes have been employed are the Mg/AgCl (used in Stingray, the British torpedo); Al/AgO (used in the SAFT lightweight torpedo, Murene); and Li/AgO (only in a developmental stage at NUSC) seawater batteries. The elements comprising a Li/AgO cell and the schematics of the Li/AgO seawater battery are shown in figure 10. Figure 11 shows a typical arrangement for a cylindrical battery employing a flowing electrolyte. Although the Mg/AgCl, Li/AgO, and Al/AgO systems do not have energy densities as high as the Li/SOCl₂ and Li/SO₂Cl₂ systems (table 3), they do have one distinct advantage: they are aqueous systems. The Mg/AgCl system simply uses seawater as the electrolyte. However, the Al/AgO and Li/AgO systems require an electrolyte reservoir. This reservoir contains a very concentrated electrolyte solution, KOH, in the case of the Al/AgO system and LiOH for the Li/AgO system. Concentrated alkaline solutions afford a very harsh environment. Consequently, these reservoirs must be made of corrosion-resistant materials. Corrosion during discharge may or may not be an issue, depending on the length of the mission. Seawater is then sucked in to dilute the electrolyte to the desired concentration. Although this requires a means of monitoring the concentration as well as mixing it to form a homogeneous solution, additional space for the water is not necessary. Consequently, a greater payload can be put in the vehicle or the vehicle can be made smaller. At the very least, the space not occupied by water, which is required to dilute the electrolyte, is made available for the pumps, heat exchangers, phase separators, etc., of the flowing electrolyte system. Powdered KOH or LiOH has been proposed instead of a concentrated solution. Although this will add less weight to the vehicle and be less corrosive than the concentrated solution, dissolving the solid electrolyte would require greater activation times. Problems with the Li/AgO, Al/AgO, and Mg/AgCl systems are that insoluble gases form as corrosion products, requiring the need for phase separators and a vent. Waste heat is also formed, which, depending on the duration of the mission, may or may not require thermal management by means of a heat exchanger. For these reasons, and because seawater is used, the Li/AgO, Al/AgO, and Mg/AgCl systems require a system using a flowing electrolyte.

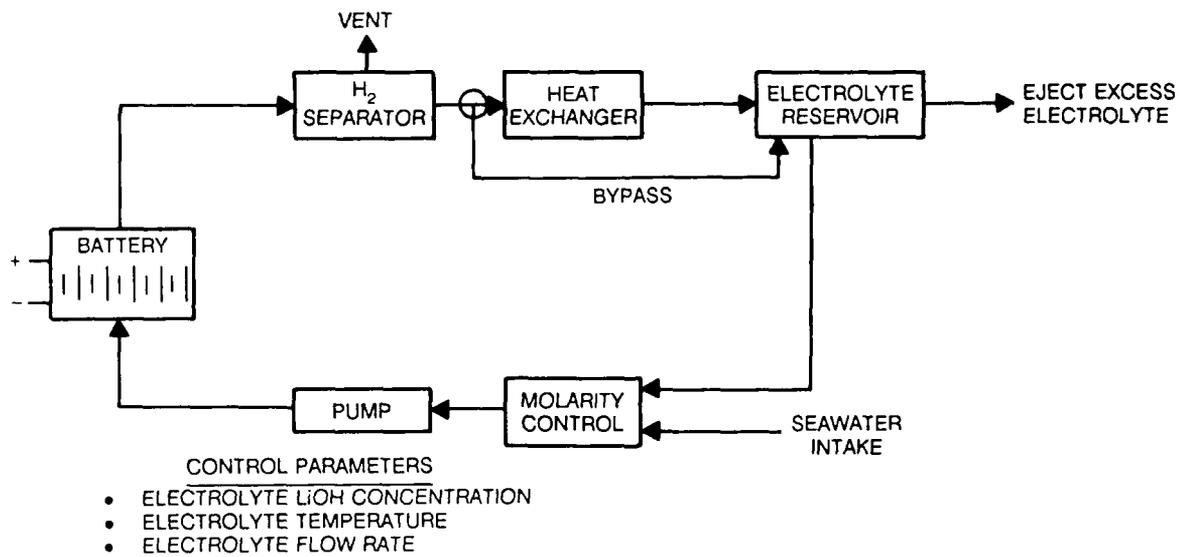
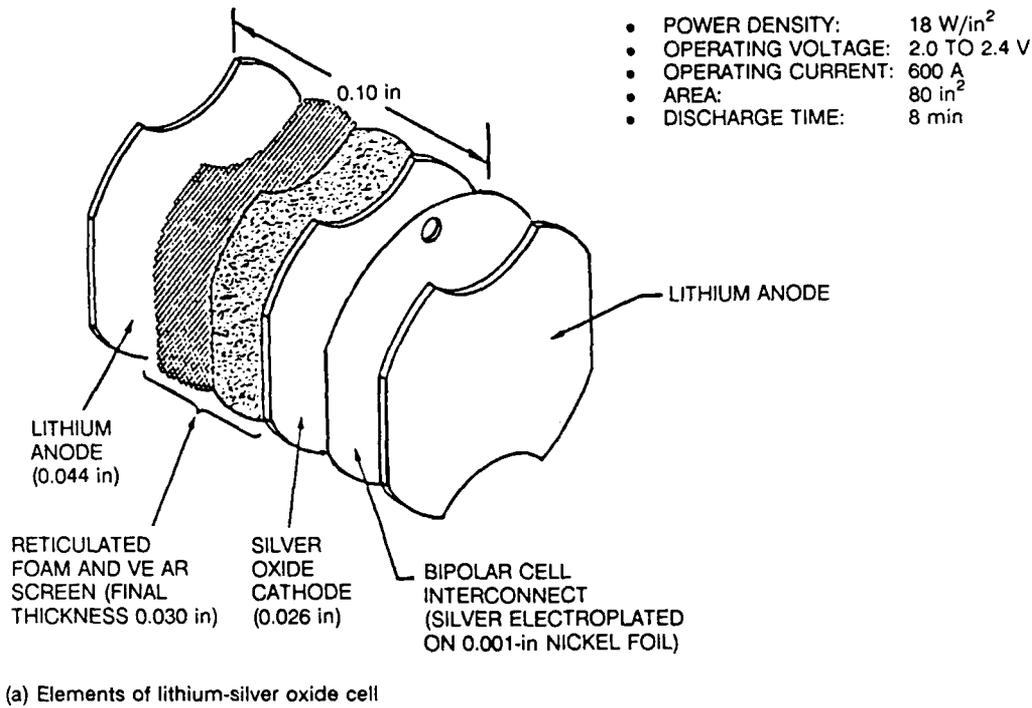


Figure 10. The Li/AgO seawater battery.

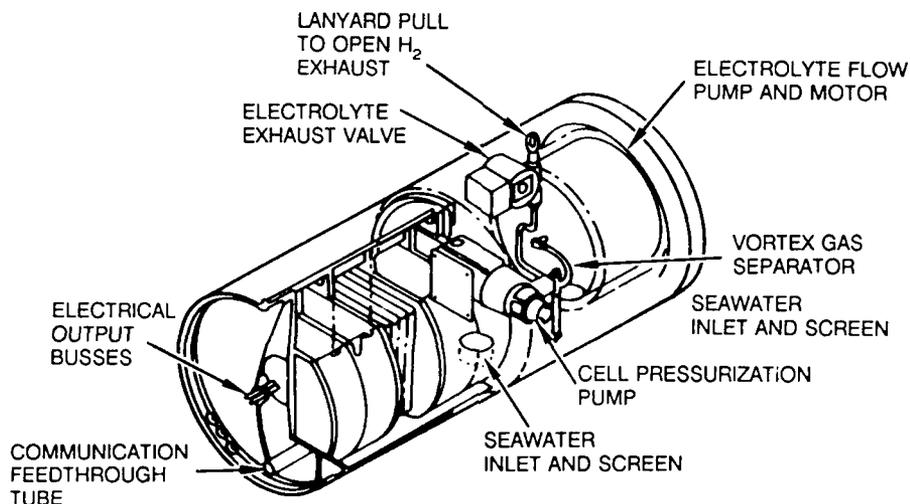


Figure 11. Typical arrangement for battery employing flowing electrolyte. Functional elements are identified.

Another problem with the Al/AgO and Li/AgO systems is the instability of AgO. The AgO component used in these reserve batteries is thermodynamically unstable and decomposes to form the lower valent state, Ag₂O, with the evolution of oxygen. This decomposition results in several performance problems during battery discharge. These include: (1) a decrease in the available discharge capacity during storage; (2) the higher ohmic impedance of Ag₂O causing voltage regulation problems upon battery activation or load application; and (3) the oxygen liberated during AgO decomposition attacking the anode, forming a metal oxide layer that inhibits rise time in reserve batteries. The decomposition of AgO during storage also inhibits performance in secondary batteries because the rate of decomposition increases in the presence of the KOH electrolyte.

4.3. NONAQUEOUS BATTERIES

The Li/SOCl₂ and Li/SO₂Cl₂ systems use nonaqueous electrolytes. Therefore, extra space must be provided for their electrolytic solutions. The electrolytes used in these nonaqueous systems are also corrosive. Again, the reservoir must be made of corrosion-resistant materials. However, during discharge corrosion may not be a consideration if the mission of the vehicle is on the order of a few minutes. As shown in figure 9, either a flowing electrolyte or a static electrolyte can be employed for these nonaqueous systems, which allows some degree of freedom in developing the propulsion system. It should be emphasized that the Li/SOCl₂ and Li/SO₂Cl₂ systems have higher theoretical specific energies and cell voltages than the seawater systems (table 3). This may compensate for the fact that the vehicle has to carry the required amount of electrolyte for the mission. Metallic lithium is stable upon immersion in SOCl₂ and SO₂Cl₂, the stability being afforded through the formation of a protective, ionically conductive film. Furthermore, SOCl₂ and SO₂Cl₂ can be reduced on carbon electrodes. Although the Li/SOCl₂ system can only be used to construct primary batteries, the Li/SO₂Cl₂ system shows some promise of rechargeability. During discharge, parasitic reactions occur in these nonaqueous systems that generate excess heat, which may or may not require thermal management. Whether thermal management is required depends on the duration of the mission. In the case of the Li/SOCl₂ system, catalysts are being incorporated in the carbon cathode to improve the

discharge performance and safety of these batteries. A great deal of this work was done by W.P. Kilroy, et al., at NSWC. It was found that a variety of materials, when incorporated in the carbon cathode or added to the electrolyte, increase cell discharge potentials and provide higher capacities at high rates. Some of the materials include finely divided Pt, Cu powder, Si, Ge, metal phthalocyanines, and related macrocyclic complexes. Table 8 presents pertinent data on some of the systems under consideration that use both solid and liquid electrolytes.

Table 8. Comparison of solid and liquid electrolyte batteries.

Couple	$E', OC (V)$	$\rho(\Omega\text{-cm})^a$	W/cm^3	Q/E^b
Li/SOCl ₂	3.32	47.6	0.28	0.68
Li(Si)/FeS ₂	1.95	0.64	5.94	0.29
Li(Al)/FeS	1.33	0.64	2.76	0.55
Ag/Zn	1.59	1.84	1.37	0.75
Na/S	2.08	4.7	0.92	0.55
Ni/Zn	1.72	1.84	1.61	0.54

^a ρ is resistivity of the solution.

^b Q/E is the ratio of thermal energy to electrical energy approximately 66% discharged.

4.4. SPECIFIC ENERGY AND SPECIFIC POWER

Frequently, the mission of an undersea vehicle requires changes in operating power level. This obviously puts a much greater demand on the battery system. The plots of specific energy versus specific power for liquid electrolyte systems show more curvature than for the molten-salt and solid-electrolyte systems, as shown in figure 7 and figure 12. This will show up in the performance of the hypothetical vehicle as it changes operational modes.

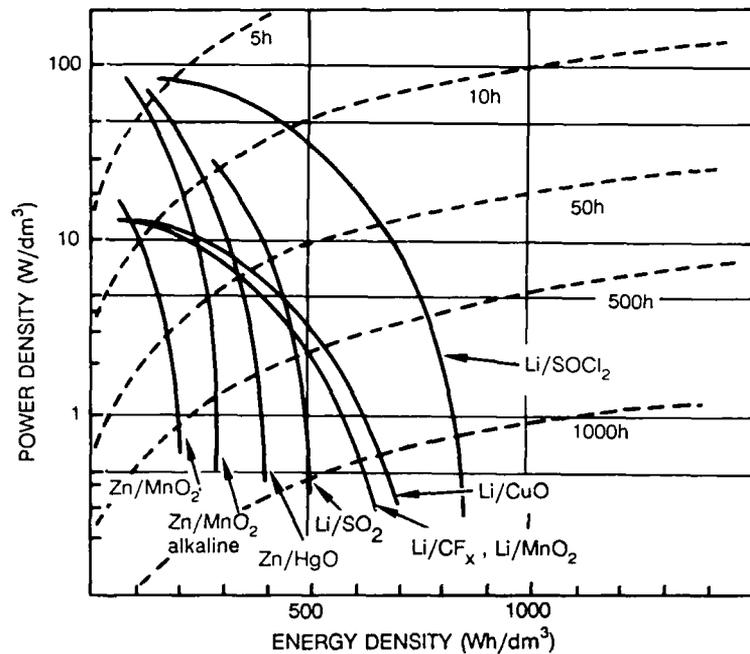


Figure 12. Specific power-specific energy curves made on volume basis for AA-size bobbin-type lithium cells compared to those for conventional cells.

4.5. STATUS OF DEVELOPMENT

SAFT has done a great deal of work in electric propulsion for undersea vehicles, including development of a power source for Murene, a lightweight torpedo using an Al/AgO flowing electrolyte system. Murene's mission has a duration of 6 to 8 minutes. The Al/AgO battery used in Murene consists of three modules. Each module, which is comprised of a bipolar stack of 30 to 40 cells, has its own circulating system. In the propulsion compartment of Murene, 50% of the weight is occupied by the cell stack, 10% by the electrolyte, and 3% by the scoop used to collect the seawater. The remainder of the weight is occupied by a gas separator used to get rid of H_2 , a hull heat exchanger, and pumps. The activation time for the Al/AgO battery of Murene is approximately 20 seconds. A thermal battery is used to run the pump, which circulates the electrolyte while the Al/AgO battery is being activated. SAFT is currently developing the power source for a heavyweight torpedo, using the Li/SOCl₂ static electrolyte system. The design of the battery is similar to the one shown in figure 9b. At this point, SAFT is testing 20-kW batteries. One major problem with the Li/SOCl₂ batteries is shunt currents.

The Li/AgO system originally was a candidate power source for the Advanced Light Weight Torpedo (ALWT). The initial work was done at the Lockheed Corp. in Palo Alto, CA. Gould, in Cleveland, OH, took over where Lockheed left off. These programs, which were terminated a few years ago, were monitored by J. Moden, NUSC, (401) 841-2411. During development, Li/AgO batteries were constructed in the form of 11-inch OD modules. These modules consisted of a number of thin cells connected in series and employed a flowing aqueous electrolyte. From an operation point of view, the system is rather complex, as shown in figure 10. However, there were no apparent problems associated with scale-up.

The Li/SOCl₂ and Li/SO₂Cl₂ systems were also candidate power sources for the ALWT. These systems were under development at Altus Corp., San Jose, CA, and at GTE, Waltham, MA. These programs were also terminated a few years ago and were monitored by S. Szpak, NOSC, (619) 553-1591, and D. Ernst, NSWC, (202) 394-1536. Both of these systems are the most energetic yet developed for practical use.

5.0. POWER OUTPUT

5.1. GENERAL CONSIDERATIONS

As can be seen from figure 3, the kinetics of chemical and electrochemical reactions determine the operational characteristics of a particular cell, including discharge rate capability and shelf storage life. This, in turn, affects power output. Battery design also affects power output; e.g., distance between the bipolar plates, thickness of the electrodes and spacers, materials used, uniformity of electrolyte flow, etc. Because of this interplay between battery design and reaction kinetics, as well as scale-up problems as one goes from a single cell to a collection of cells, it is difficult to predict with any reliability the size battery needed to produce the desired amount of power under a specified set of conditions. To be able to do so requires extensive research into the candidate systems (computer modeling, basic research on the electrochemical and chemical processes occurring within the cell, etc.). What follows is a very general discussion of power output from a single cell. (Szpak and Driscoll, 1987; Mosier-Boss et al., 1987).

In general, the power output of a cell is given by equation 1:

$$P = iV \quad (1)$$

where P is power in watts, i is current in amperes, and V is the working, or operating, cell potential in volts. Equation 1 assumes that, for a given period of time, i and V do not vary. However, in most cells, during constant current discharge, cell potential decreases with time as shown in figure 13. Consequently, equation 1 is best represented by the following expression:

$$P = i \int V dt \quad (2)$$

In a cell discharging at a constant current density, j in mA/cm², i can be calculated as follows:

$$i = 0.001 jA \quad (3)$$

where A is the area of the electrode in cm² and 0.001 converts mA to amperes. Comparing equation 1 and 3, one must either increase the working cell potential, V , or increase the discharging current density, j , to increase the power output of a cell. The working-cell potential, V , is the open-circuit potential, V_o , less all of the losses associated with the electrode reactions and transport processes, shown in figure 3,

$$V = V_o - \sum_{\kappa} \Delta\mu_{\kappa} \quad (4)$$

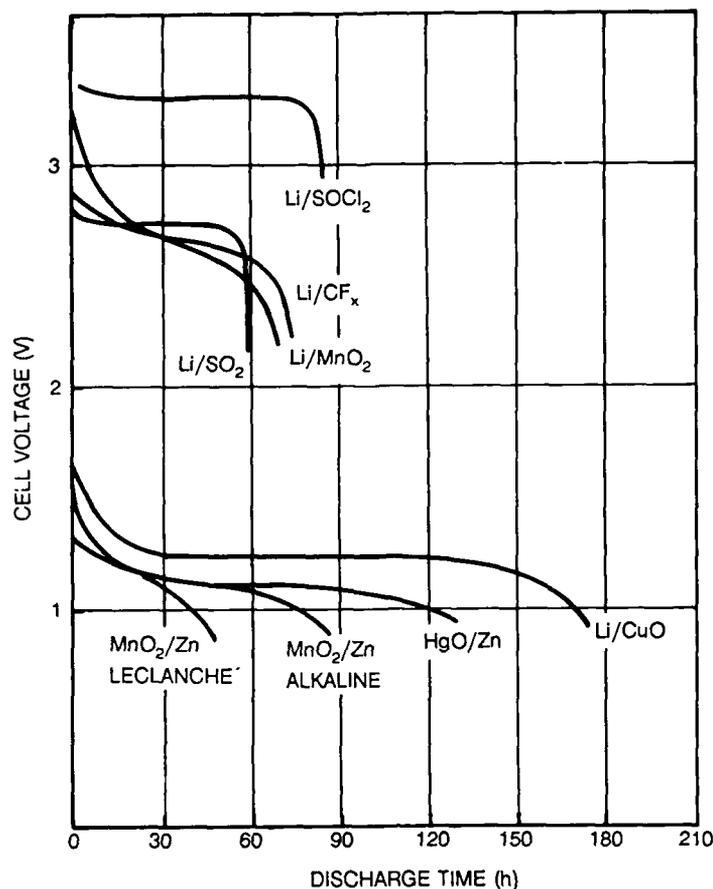


Figure 13. Discharge characteristics of AA-size non-aqueous solid and liquid lithium cells under 20-mA continuous drain, compared to those for traditional cells.

where $\Delta\mu_k$ is the driving force for the k -th process expressed in volts. Equation 4 indicates that the working-cell potential depends on mass transport and the other processes occurring during discharge. These, in turn, depend somewhat on the design of the battery as well as the kinetics of charge transfer, adsorption of electroactive species, etc. The same is also true for the discharge current density, j . The working-cell voltage is also dependent on the open-circuit potential, which is inherent with a particular redox couple. Therefore, V and j can be changed by switching redox couples, by modifying the kinetics of discharge, by modifying the transport of reactants and products, etc. Again, there is a very strong interplay between the kinetics and thermodynamics of the reactions occurring in the battery and the battery's physical design.

5.2. POWER OUTPUT FROM A MODULE

As discussed earlier, the Li/SOCl₂ system has a very high density and high cell potential. It is also the battery system with which the authors of this report have the most familiarity (Szpak and Driscoll, 1987). Therefore, it will be used as an example in discussing volume requirements within a vehicle. In a developmental effort encompassing the years 1982 to 1985, modules consisting of 86 cells were made and discharged. These modules were cylindrical in shape and had an 11-inch diameter. The bipolar stack of cells occupied

approximately 1 inch of the length of the cylinder. An additional inch was required for the electrolyte, which, as discussed earlier, is in a reservoir. The overall potential of each module is approximately 280V. A typical discharge curve for a module, in which the rate of discharge is approximately 80 mA/cm^2 , is shown in figure 18. Therefore, one Li/SOCl_2 module provides 9 kW of power. The volume occupied by this module is 190 in^3 . Additional volume is required for the activation system, which will deliver the electrolyte to the bipolar stack. How much additional volume is required depends on which delivery system is used; e.g., a pump, a piston, etc. Note that each module weighs approximately 6.5 kg.

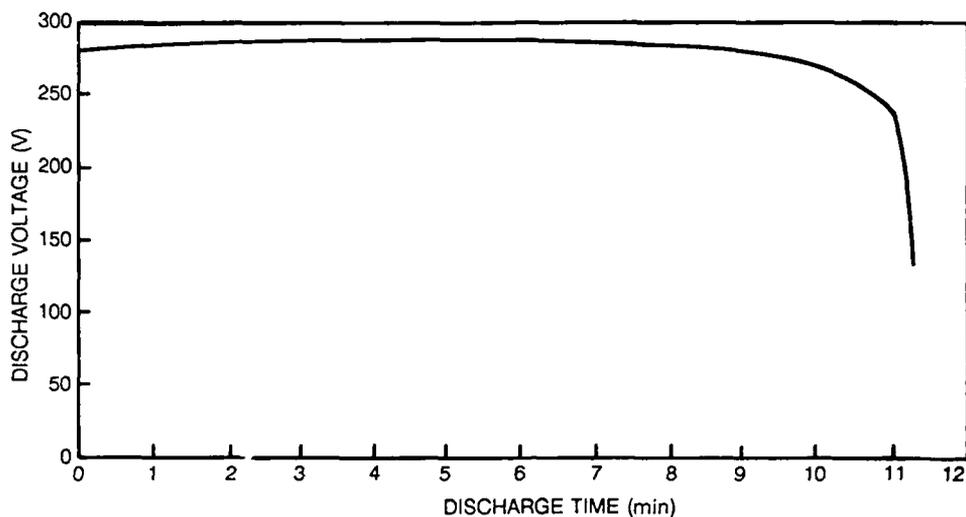


Figure 14. Typical discharge curve for a Li/SOCl_2 module discharged at approximately 9 kW. Each module consists of 86 cells.

5.3. SCALE-UP PROBLEMS

Battery scale-up problems associated with construction and manufacturing processes can be summarized by the statement that a good battery must ensure the following: controlled spacing of all active cell components, elimination of intercell currents, reliable contact between the electrolyte and electrodes, minimum ohmic losses within the battery, and uniform electrode loading (Mosier-Boss, et al., 1987; Parnell and Szpak, 1985; Szpak et al., 1987).

To maximize the energy density, cells must be thin and, to achieve the required power density, a great number of such cells must be placed in series. However, as these cells become thinner, the difficulty in maintaining the required uniform separation of the active components increases. Similarly, as the number of cells in a module increases, intercell currents present a serious problem because of a reduction in cell efficiency, often resulting in cell module failure. As the linear dimensions of a cell increase, effective contact between the electrolyte and the electrodes is less certain, especially when gaseous reaction products are formed in the course of battery discharge. With the increase in battery size, the fabrication of electrodes having uniform reactant loading is also more difficult. Batteries employing flowing electrolyte (e.g., Li/AgO and Al/AgO systems) are provided with heat exchangers; consequently, heat management in such an operating module is under active control and there is no limit on linear dimensions except as may be required to maintain

the electrolyte composition within an acceptable range. A more serious problem is encountered with an increased number of cells in a module owing to the difference in the flowrate in end cells. This is of particular importance in Li/AgO systems because the cell output is sensitive to flowrate. Thus the number of series-connected cells is limited by hydraulics considerations. A module usually contains about 50 cells for the Al/AgO system and somewhat fewer for the Li/AgO.

Intercell current is an ionic current that originates in one cell and terminates in another. Such a current does not perform any useful work and is, in fact, parasitic. In particular, these intercell currents cause power loss, current inefficiency, and nonuniform cell-to-cell current distribution. They may also contribute to the premature failure of individual cells by the corrosion of structural parts, by the formation of passive films, and by initiating dendritic growth that might lead to catastrophic thermal runaway. Not surprisingly, the magnitude of the intercell current is a function of the number of cells in the assembly, the cell voltage, the conductivity of the electrolyte, and the geometry of the electrolyte feed system.

Scaling batteries to larger sizes, and consequently increased total energy, has significant effects on thermal management of these power sources. The main source of heat generation in batteries is attributed to the polarization of individual electrodes and the internal cell resistance. Occasionally, additional heat sources have been identified (e.g., as the result of intercell current, always present in the reserve-type batteries, and to chemical reactions between the cell components and reaction products). These additional heat sources may create conditions of thermal runaway, which is characterized by self-acceleration resulting from the accumulation of heat. In essence, thermal runaway is the inability of a system to transport sufficient heat to the environment to maintain thermal stability. Note that energetic batteries operating at high power outputs are susceptible to thermal runaway, which, particularly in Li batteries, often yields temperatures exceeding the melting point of the casing material. The result is an uncontrolled, violent reaction. Furthermore, these reactions may be caused by localized heat sources arising from defective cells and/or cell components, and can occur anytime during activation and discharge.

6.0 CONCLUSIONS

6.1. SUMMARY

The optimum system to propel an undersea vehicle is one that yields a high power output regardless of the operational mode of the vehicle. This, in turn, means that the system has a high cell potential as well as a horizontal V -versus- t profile during high rates of discharge. It is desirable to have a linear relationship between specific energy and specific power. Because of size constraints, the system also has to be light in weight and take up very little volume.

6.2. CURRENT STATE OF DEVELOPMENT

1. An Al/AgO system has already been fully developed by SAFT. It is not as powerful as the other systems discussed.
2. Zn/AgO has high power but not much energy density. It would be good for missions of short duration. Development of a Zn/AgO system should be straightforward. Much of what was learned in the development of the Al/AgO system should be applicable for Zn/AgO.

3. Li/AgO is powerful but energy poor. Gould, Ocean System Div., Cleveland, OH, which is now owned by Westinghouse, did have a program to develop this system. However, the current status of development is unknown.
4. Li/SOCl₂ is both a high-power and a high-energy system. It is currently being developed by SAFT. Some developmental work was contracted by NOSC to Altus, San Jose, CA in the early 1980s.
5. Thermal (i.e., molten-salt and solid-electrolyte) batteries, to date, are experiencing scale-up problems because of thermal runaway. At this time, it is difficult to say whether these problems can be overcome. Development is being carried out by SAFT of America and Catalyst Research.

6.3 SAFETY

In all electrochemical systems, safety is an issue. Whenever you have a great deal of energy stored in a small package, there is a potential for a catastrophic event. Rigid quality-control procedures must be developed and observed to ensure the safety of the people handling the battery and the vehicle before and after completion of the mission. Of the systems under consideration, the Al/AgO and Zn/AgO batteries are generally regarded as being safe. Some incidents have been reported with the Li/AgO system, although the causes are not yet understood. Incidents have also occurred with the Li/SOCl₂ system. However, computer modeling has revealed the causes of Li/SOCl₂ incidents and they are avoidable with good quality-control procedures. In the case of molten- and solid-electrolyte batteries, thermal management is a major problem. With inadequate thermal management, thermal runaway can occur, with its usual catastrophic results (Szpak and Driscoll, 1987; Chemical Division, 1989; Momyer and Littauer, 1982).

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