

Silver Zinc Batteries for AUV Applications

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ABSTRACT

Silver-Zinc batteries have been in use for years in many underwater applications. With the advent of AUVs, silver-zinc has been chosen to supply the power for various applications. Although a specialized niche, the silver-zinc electrochemistry offers advantages in size and power that are critical to certain applications.

INTRODUCTION

Silver-Zinc batteries have been used in numerous submersible vehicle applications, both autonomous and manned types. Examples of both are listed below:

AUV Applications

- MK 30 - Torpedo Target (190AH cell)
- MOSS - Mobile Submarine Simulator (140AH cell)
- Draper/DARPA UUV (1200AH)

Manned Submersible Applications

- DSRV, Deep Submergence Rescue Vehicle (700AH cell)
- DSV Deep Submergence Vehicle, Alvin (750AH cell)
- NR-1, Nuclear Research Submarine (850AH cell)
- SDV, Seal Delivery Vehicle (365AH cell)
- ASDS, Advanced Seal Delivery Vehicle (740AH cell)

There are many advantages to silver-zinc that make it the electrochemistry of choice for critical applications. High volumetric and gravimetric energy density are two of these key selection factors. The ability to support high rate discharges, up to 1 amp/in² (Power Density) and a linear voltage over almost the entire range of its discharge also make it desirable for many applications. Silver-zinc also possesses excellent charge retention, electrochemical efficiency and low temperature performance. Its excellent safety record and relatively benign failure modes also make silver-zinc an attractive selection.

However, there are tradeoffs with any technology and silver-zinc has its limitations. The chemistry has a relatively low cycle life of between 50 and 100 cycles and wet life is limited to between 12 and 18 months. Existing designs are vented, dictating that gas management may be a factor

depending on the application. Silver-zinc also does not tolerate overcharge or over-discharge well.

Table I is a comparison of typical energy densities for cells of common rechargeable electrochemistries. The point of this comparison is to illustrate the relative energy densities. Improvements are being made to other chemistries, but to date, silver-zinc has the highest energy density among rechargeable batteries.

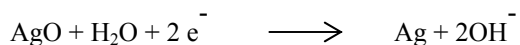
Table I
ENERGY DENSITIES OF RECHARGEABLE BATTERIES

Chemistry	Gravimetric (Wh/kg)	Volumetric (Wh/l)
Pb-Acid	30-45	60-100
Ni-Cd	40-65	70-100
Ni-H ₂	40-60	70-90
Ni-MH	60-80	100-140
Ni-Zn	60-80	120-160
Ag-Cd	70-100	140-200
Li-Ion	115-160	250-360
Ag-Zn	140-200	400-510

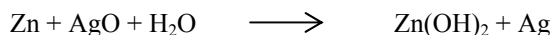
Although there are many complexities in the details of the operation of a silver-zinc cell, from a larger perspective, the oxidation-reduction reactions are relatively simple. During discharge oxidation occurs at the negative (zinc) electrode.



Reduction occurs at the positive (silver) electrode.



The overall cell reaction involves the transfer of oxygen from the silver electrode to the zinc electrode using the hydroxide ion from the potassium hydroxide electrolyte as the transfer medium. This reaction is reversible.



These reactions along with the material and process variables applied to the design and fabrication of the cell electrodes, determine the performance characteristics of the chemistry.

ELECTRODE FABRICATION TECHNIQUES

Silver electrodes can be fabricated in the uncharged (Ag) and charged (AgO) forms by combining them with a silver current collector. Uncharged electrode fabrication techniques include taking silver powder and pressing or rolling it to achieve a particular density and thickness followed by sintering for strength, vs. using a pasted silver monoxide (Ag₂O), which is then sintered to drive off the oxygen and binder while adding strength. Charged electrodes are fabricated by taking sintered silver electrodes and electrolytically forming them. Other techniques involve taking silver monoxide (Ag₂O) or peroxide (AgO) powders and pasting or roll bonding them to silver collector materials using binders.

Zinc Electrodes are also fabricated in both the uncharged (ZnO) and charged (Zn) states. The method chosen for a particular design depends on the performance characteristics required for the battery application. Typically for long cycle life, deep discharge applications, uncharged zinc-oxide electrodes are used made by combining ZnO powder with binder and dry pressing or pasting as a slurry. Charged zinc electrodes are made by pressing zinc metal powder with binder, plating zinc metal from solution onto a collector or by electroforming pressed or pasted zinc-oxide powder plates made as described above.

SEPARATOR MATERIALS

Separator materials are employed to keep the silver and zinc electrodes from shorting to one another. A variety of separator materials have been used in silver-zinc cells over the years. The most common and successful separators are the cellulose. Battery grade cellophane is widely used and offers proven performance at a reasonable cost. Wet life and cycle life of a cell design can be tailored to meet the requirements of an application by varying the number of layers of cellophane between electrodes. When the application calls for it, fiber reinforced sausage casing is used in place of or in combination with cellophane to provide a more rugged separator system. Cost and handling issues inhibit the more common use of fibrous casing. The down side of cellulosic separators is that they are susceptible to attack from the silver oxide electrode and the potassium hydroxide electrolyte, which contributes to the limited wet life and cycle life of the chemistry.

Various polymers, such as poly-vinyl-alcohol (PVA), and grafted and irradiated polypropylene have been developed for use in silver zinc batteries in recent years. Polymer separators offer better chemical resistance to electrodes and electrolyte but issues with wettability, low conductivity,

temperature limitations and cost have prevented the more widespread use of these materials in silver-zinc designs.

ELECTROLYTE

A 40 to 45 % weight solution of potassium hydroxide (KOH) with water is typically used as the electrolyte in silver-zinc cells. The weight percent would be varied to balance conductivity and life requirements of the application, with a 40% solution offering higher conductivity, but attacking the separator more quickly.

Electrolyte levels of silver-zinc cells vary as a function of the state of charge. The temporary disappearance of electrolyte when a cell is discharged is due to the combining of some of the water and hydroxides of the electrolyte with the zinc in the discharged negative electrode in the form of zinc hydroxide. When recharged, the water and hydroxides will be released raising the electrolyte to its original level.

Electrolyte may permanently disappear from the cell over time through via gassing on open circuit stand or during over charge and over discharge. Gassing splits the water in the electrolyte and allows it to be removed from the cell by venting.

GASSING MECHANISMS

All silver zinc cells generate gas. During charged stand and discharge, the majority of gas is hydrogen. This is due to a corrosion reaction, which takes place at the zinc electrode. The zinc corrodes or self discharges to zinc hydroxide by reacting with the KOH and water in the electrolyte and releasing hydrogen in the process. Small percentages of lead, cadmium and mercury are added to zinc electrodes to inhibit this corrosion reaction. Some oxygen will be generated on stand, but the rate of this reaction is not significant at temperatures less than 110°F.

At end of charge, oxygen is evolved at the silver electrode and hydrogen is evolved at the zinc electrode due to the splitting of the water in the electrolyte. Reversal, or over discharge will also split the water in the electrolyte, but the gasses will evolve at the electrodes opposite of over charge. Both overcharge and reversal are detrimental to cell performance due to effects on electrolyte, separator and electrodes.

VOLTAGES OF THE SILVER ZINC CELL

Under no-load or open circuit conditions the silver-zinc cell has two distinct voltages. When fully charged to zinc and silver peroxide, the cell exhibits an open circuit voltage of 1.86 volts nominal. When partially discharged, more than 30% capacity out, the cell will exhibit an open circuit voltage of 1.60 volts nominal.

Under typical discharge loads, the silver-zinc cell has a plateau voltage of 1.50 volts nominal. This plateau will be slightly higher under low load conditions and lower under high current loads. At the start of discharge of a fully charged cell, the voltage will be approximately 1.7 volts and continually drop until it reaches the 1.5 volt plateau when about 15 to 30 % of the capacity has been removed.

When charging a fully discharged silver-zinc cell, voltages will start out at approximately 1.65 volts for the first 15 to 25 % of the charge. At this point the cell voltage will rise to a second plateau of 1.95 volts. As the charge continues and all of the silver in the positive electrodes is converted to silver oxide, the voltage will rise to a third plateau of 2.05 volts. This third plateau is an indication of full charge at which time the charge should be stopped, as oxygen will begin to evolve from the positive electrode if the charge is allowed to continue.

FACTORS INFLUENCING BATTERY LIFE

Numerous factors, many of which can be controlled by the user, effect the useful life of a silver-zinc battery. As such operational and maintenance procedures are critical to maximizing the performance of silver-zinc batteries in the field. Factors having a positive effect on performance and life are as follows:

- Shallow Capacity Discharge Cycling < 75%
- Low Current Discharges - Less than "1-C" Rate
- Moderate Temperature Operation
- Low Temperature Storage < 40°F
- Full Charge Cut-off at Recommended Voltage
- Low Rate Charge
- Regular Maintenance

Conversely, these negative factors will have a detrimental effect on silver-zinc battery life and performance:

- Deep Capacity Discharge Cycling > 75%
- High Current Discharge > "1-C" Rate
- High Temperature Operation
- High Temperature Storage > 125°F
- Overcharge
- High Rate Charging
- Cell Reversal (over discharge)

Failure modes common to silver-zinc cells and batteries include capacity loss due to negative electrode shape change and shorting due to zinc shorts, silver shorts or a combination thereof through the separator system. Causes of these failure modes could be normal such as age (end of wet life, deterioration of the separator system). However, premature failures may occur due to abuses such as the negative factors previously cited.

CELL CHARACTERISTICS

Silver-zinc cells with capacities ranging from 1 to 2000 ampere-hours in size are similar in design and construction. They have a prismatic cell geometry, which provides for a good packing factor in most applications. Cell cases and covers are made of injection molded plastics such as polysulfone, ABS, SAN, and polypropylene. Polysulfone is preferred for its high temperature performance and high strength properties. The use of polysulfone, with its ability to withstand high temperatures helps to mitigate propagation of short circuits throughout a battery should a hot short occur in one cell.

Connections to electrode leads are made using brass or steel terminals and using solder or crimp methods. "Standard Construction" silver-zinc cells are pressurized and must be kept within the pressure hull of the AUV or submersible vehicle. "Pressure Compensated" designs are open to seawater pressures and are located outside of the vehicle pressure hull.

"Standard Construction" cells within the pressure hull are closed with a vent valve to relieve internal pressure. This type of cell design has a relatively short headspace between the top to the electrodes and the bottom of the cell cover and intercell connections are simple copper strip buss bars bolted between cells. This type of cell may be built as a dry charged cell, which is shipped dry, ready to use after the electrolyte is added. It may also be built in the green state (uncharged) in which case the cells or battery must be activated and charge/discharge cycled a few times to condition the cells prior to field use.

"Pressure Compensated" cell/battery designs are open to ocean depth pressure and therefore have no relief valve. They are protected from seawater with a layer of mineral oil on top of the cells and battery. This mineral oil layer keeps the seawater and electrolyte from contacting one another and the level of this oil fluctuates in the cell with the changes in water pressure. The cells incorporate a tall headspace to allow for the fluctuation in oil level without contaminating the electrode pack. As the tops of the battery cells are immersed in mineral oil, intercell connections must be made using rubber coated cable with sealed contacts.

Table II summarizes the size and performance characteristics for silver-zinc cells used in submersible applications, both standard and pressure compensated types.

BATTERY CHARACTERISTICS

A variety of materials, such as fiberglass, stainless steel, aluminum and titanium are used to fabricate battery cases for silver-zinc cells. The selection is based on the needs of the particular application. Some applications do not require a battery case and cells are simply restrained by wrapping or

Table II
SILVER-ZINC CELL CHARACTERISTICS

Parameter	Cell Model								
Nominal Capacity	140 AH	190 AH	365 AH	700 AH	740 AH	750 AH	850 AH	1200 AH	1800 AH
Initial Capacity	164 AH	200 AH	525 AH	920 AH	740 AH	950 AH	1100 AH	1300 AH	2250 AH
Height	17.4 cm	16.3 cm	18.7 cm	48.0 cm	18.7 cm	49.6 cm	48.0 cm	30.2 cm	58.9 cm
Width	8.4 cm	15.1 cm	14.8 cm	10.7 cm	16.0 cm	14.2 cm	12.0 cm	14.5 cm	13.6 cm
Depth	5.6 cm	3.9 cm	7.0 cm	10.7 cm	8.0 cm	9.7 cm	11.5 cm	10.8 cm	13.3 cm
Volume	0.82 L	0.96 L	1.94 L	5.49 L	2.39 L	6.79 L	6.62 L	4.71 L	10.65 L
Wet Weight	1.62 kg	2.00 kg	4.00 kg	11.70 kg	5.67 kg	12.50 kg	13.60 kg	11.40 kg	21.80 kg
Discharge Current	30 amps	47 amps	60 amps	140 amps	20 amps	150 amps	170 amps	60 amps	220 amps
Volumetric Energy Density	301 wh/L	313 wh/L	406 wh/L	252 wh/L	464 wh/L	210 wh/L	249 wh/L	414 wh/L	317 wh/L
Gravimetric Energy Density	152 wh/kg	150 wh/kg	197 wh/kg	118 wh/kg	196 wh/kg	114 wh/kg	121 wh/kg	171 wh/kg	155 wh/kg
Cell Type	std.	std.	std.	PC	std.	PC	PC	std.	std.

strapping the battery pack, which is installed directly into the vehicle's battery compartment.

In most applications the battery consists of a group of series connected cells, and usually contains a power connector assembly, although some designs have only positive and negative battery taps that are hardwired to the vehicle. Individual cell voltage monitoring (ICVM) connector assemblies are used to facilitate charging and maintenance activities and if the vehicle electronics support, can be used to insure discharge cutoff prior to cell voltage reversal.

All batteries with sealed cases incorporate vent relief valves. In batteries open to water pressures, a pressure compensation system is included.

PERFORMANCE CHARACTERISTICS

Silver-zinc cells and batteries withstand storage and non-operating temperatures as low as -20°F and as high as +140°F. The minimum practical operating temperature is between zero and 20°F depending on the discharge rate and voltage required. High temperatures are not a concern as long as the end of discharge temperature of the battery does not exceed 200°F for prolonged periods of time.

Silver-zinc batteries have proven performance under a wide range of pressure environments from full vacuum to 20,000 ft H₂O. They also have demonstrated tolerance to many dynamic environments such as standard transportation and shipboard vibration. Cells must be maintained in the upright orientation during charging, but any orientation including temporary inversion is acceptable for discharge.

OPERATIONAL REQUIREMENTS

Requirements for proper operation of silver-zinc batteries include vehicle integration and support operations. Access to batteries for re-charge is essential and the vehicle must include considerations for thermal and gas management. At a minimum, onboard electronics must be capable of accurate and reliable battery voltage and current monitoring. For large and complex batteries, cell voltage monitoring capability is also required. The electronics must also be able to record ampere-hours removed from the battery.

Support operations and equipment requirements include a vacuum system for cell activation and maintenance procedures and electronics, power supplies and load banks for charging and discharging the batteries. Ideally lab or field equipment should include electronics capable of monitoring individual cells to permit top charging of individual battery cells at least once every 10 cycles

USER SELECTION GUIDELINES

Off the shelf designs offer the best cost and schedule benefits, but usually require compromises in performance and fit. Tailored designs using existing tooling can custom match the cell design to the vehicle's performance requirements, but may still require compromises in fit. Custom designs provide the best match to fit and performance requirements, but come with higher non-recurring engineering costs and longer development cycles.