Silver based batteries for high power applications

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Abstract

The present status of silver oxide–zinc technology and applications has been described by Karpinski et al. [A.P. Karpinski, B. Makovetski, S.J. Russell, J.R. Serenyi, D.C. Williams, Silver-Zinc: status of technology and applications, Journal of Power Sources, 80 (1999) 53–60], where the silver–zinc couple is still the preferred choice where high specific energy/energy density, coupled with high specific power/power density are important for high-rate, weight or size/configuration sensitive applications.

Perhaps the silver oxide cathode can be considered one of the most versatile electrode materials. When coupled with other anodes and corresponding electrolyte management system, the silver electrode provides for a wide array of electrochemical systems that can be tailored to meet the most demanding, high power requirements. Besides zinc, the most notable include cadmium, iron, metal hydride, and hydrogen electrode for secondary systems, while primary systems include lithium and aluminum. Alloys including silver are also available, such as silver chloride, which when coupled with magnesium or aluminum are primarily used in many seawater applications.

The selection and use of these couples is normally the result of a trade-off of many factors. These include performance, safety, risk, reliability, and cost. When high power is required, silver oxide–zinc, silver oxide–aluminum, and silver oxide–lithium are the most energetic. For moderate performance (i.e., lower power), silver oxide–zinc or silver–cadmium would be the system of choice.

This paper summarizes the suitability of the silver-based couples, with an emphasis on the silver–zinc system, as primary or rechargeable power sources for high energy/power applications. © 2000 Elsevier Science S.A. All rights reserved.

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1. Background

A capacitor stores energy in an electric field. In contrast, a battery stores energy in the chemical reagents formed during the charging process. Upon discharge these chemicals then react to produce an electric current. The resistance of the electrolyte initially controls the rate of discharge of a storage battery. As the surface energy is depleted, discharge rates become dependent on chemistry and ion diffusion within the active layer. For thin cell batteries with properly formed active layers, discharge rates can be tens of amperes per square centimeter and discharge times can be hundreds of microseconds.

In 1924, P.L. Kapitza [1] developed a thin cell battery comprised of lead plates and sulfuric acid as part of his work in high intensity pulsed magnetic fields. He achieved a peak power of 1 MW in a 0.09 m^3 volume for a power density of 11 MW/m^3. The Armour Research Foundation reviewed this same system for an electric gun application in a 1947 report [2]. Since that time, silver-based batteries have also been used or considered as an option on similar programs. Many of these have been for missile or torpedo applications. For example, as part of a study performed for the Army Armament Research and Development Command, Picatinny Arsenal, in 1985, 140 A h silver–zinc cells designed for the MK 104 torpedo, were successfully discharged for hundreds of milliseconds at approximately 1.24 A/cm^2. For most other programs, discharge rates between 0.08 to 0.4 A/cm^2 are typical for the rated nameplate capacity of the cell.

1.1. Design philosophy

Regardless of electrochemical couple, the design of any cell is the result of a compromise between numerous and often conflicting demands. Among these are size, weight,

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capacity, discharge rate, wetstand life, cycle life, environmental exposure, safety, and other special requirements. With high specific power and energy output of prime importance, the design trade-offs must be examined closely.

In order to maximize the power output of a cell, the internal resistance must be reduced. The primary methods of reducing the internal resistance are as follows:

· increasing the electrode surface area;
· reducing the separator thickness;
· reducing the electrolyte/separator material resistivity; and
· decreasing the resistance of current carrying components.

When increasing the total electrode area, the combined internal resistance of the electrolyte and separator is reduced proportionately. However, if the electrodes cannot be manufactured any thinner, the weight of the electrode (along with the electrolyte and separator weight) must be increased proportionately. Therefore, a key element to achieving high power density outputs is the manufacture of thin layers of active material.

Reducing separator thickness reduces the length of the electrolyte/separator path, through which current must pass and, consequently, reduces the cell's internal resistance. This must be done without significantly affecting the primary separator functions of preventing internal shorting and serving as an electrolyte reservoir.

Electrolyte resistance may be reduced by changing the concentration or by introducing certain additives. For example, for potassium hydroxide, which is most commonly utilized as an electrolyte in the systems considered, concentrations around 28% offer the least resistance. However, this concentration may not be ideal because of accelerated oxidation of some separators and polarization at very high discharge rates.

The electrical resistance of current-carrying cell components can be decreased by using sound design practice. In essence, this is achieved by designing shorter current-carrying paths and larger cross-sectional areas where required. Furthermore, some battery constructions (i.e., pile or hybrid batteries) have a significant built-in advantage in this respect.

If we consider the specific power requirements alone, conventional high rate silver oxide–zinc cells may approach 1.47 to 1.82 kW/kg. This specific power yield can be improved to 3.7 to 4.35 kW/kg by utilizing thin electrodes and state-of-the-art thin separator systems. By resorting to pile battery construction and bipolar electrodes, further improvements would result in a power output of approximately 5.56 kW/kg. Even though the specific energy of nickel–cadmium is less than that of the silver oxide–zinc system, it is similar to it in terms of power capability. The adverse effect of the much heavier nickel and cadmium electrodes is compensated by the use of simple, low electrolytic resistance separators allowing higher currents to be attained. This is possible because of the high stability of both electrodes, in part due to their low solubility in the electrolyte. As a result, nickel–cadmium could also achieve power densities of 4.34 kW/kg by resorting to thin electrode construction.

It is essential to note that the power output challenges cannot be resolved without considering the full spectrum of requirements, which includes supplying the necessary energy for the duration of the intended mission. In this area, the silver oxide–zinc system offers a decided advantage: its energy density is higher than that of nickel–cadmium by a factor of better than 2 to 1.

The cathodes of the silver–zinc cells may be charged to two different states of oxidation: the silver peroxide (divalent), with an open circuit voltage (OCV) of 1.86 VDC and the silver monoxide (monovalent), with an OCV of 1.60 VDC. During low rate discharge of a fully charged cell, the transition to the monoxide level occurs at approximately 60% of the cell capacity. Although it seems natural to use 100% of the available capacity, to operate at the monoxide level offers the following advantages.

(1) The high rate pulse voltage is more stable, especially after prolonged stand in the charge condition. In that condition, the silver peroxide tends to react with the silver grid to create a highly resistive monomolecular layer of silver monoxide at the powder-grid interface. This layer is quickly broken during cell discharge, but may create a low power condition for a period of time extending from milliseconds to perhaps a few seconds. Silver monoxide, however, does not react with the grid and furthermore it always contains particles of pure silver mixed in, thus no high resistance layer is ever formed.

(2) The absence of silver peroxide removes one of the main threats to the life of the separators, thus insuring a longer wet life and cycle life for the cell.

Furthermore, the resulting energy output degradation of a monoxide design is not as significant as might first appear. The design is typically optimized to account for this mode of operation by reducing the amount of negative active material and using the resulting available space to increase the active material of the silver electrode.

2. Results and discussion

Over the years, special high rate, short duration tests were conducted on various standard Yardney high rate cells. Although some of these were short circuit tests, where the voltage drops to near 0 V, the peak power current can be calculated from the short circuit current. Assuming that the relation between voltage and current is linear, the peak power current is exactly one half of the short circuit current. For example, two parallel banks of Yardney model HR140DC cells, normally used for torpedo and torpedo-target propulsion, were able to deliver in

excess of 5500 A. This represents a peak power current of over 2750 A, corresponding to a current density of more than 0.62 A/cm^2.

Table 1 summarizes various battery configurations that provided some of the highest energy outputs tested to date. Of those listed, special evaluation studies were also conducted in order to characterize the capability of the battery, and in many cases, new electric propulsion systems. One such program by the US Navy was to develop a fast and deep mobile target [3].

Because of time constraints, the Naval Underwater Weapons Center (NUWC) was tasked to evaluate a cell that was readily available for this study. A series of high- and low-rate tests were run, while selecting 850 A as the desired high-speed operating point of the motor. The results of this program have shown that the HR 190 DC cell in its present form is capable of delivering the power required to support the fast target program. One general observation on this and other similar programs was the higher end-of-discharge temperatures obtained during the high current discharges. In most cases, this condition did not have a catastrophic effect on the battery except a reduction in the life. Refer to Figs. 1 and 2 for polarization data and comparison of electrolyte molarity. A brief summary of other programs is outlined below.

2.1. Special test programs

An evaluation was made from a bank of series/parallel configured HR140DC cells for a potential rail gun applica-

tion. After the application of a dead short across the battery, the cells were able to draw instantaneously 20 000 A [4]. A similar test program was also run on PML110 silver–zinc cells that operated at over 2 A/cm^2. Fig. 3 is typical of a series of short duration pulses with the corresponding cell voltage at around 0.1 VDC. If the load were allowed to remain on the cells, the typical failure mode would simply consist of the electrode leads fusing open, usually in 30 s or less [5].

2.2. Launch vehicles, boosters, and missiles

These include smaller batteries of limited wet life designed for a high rate of discharge from a few amperes to over 2000 A for short duration pulses. The cell voltage regulation is very stringent and usually requires processing of the silver electrodes in the monovalent state. The vehicle dynamic environments are the most demanding, where random vibration and pyrotechnic shock levels are normally the highest of all applications (e.g., typically 50 to over 100 g in vibration and over 10,000 g's in shock).

2.3. Underwater vehicles, torpedoes, and targets

Although the rate capability requirements are similar to those of the Launch Vehicle, Booster, and Missile battery applications, the underwater batteries tend to be larger due to the increased capacity requirements (i.e., minutes and hours versus seconds) and are capable of being recharged

Table 1
Battery configurations

Program	System design	Capacity (A h)	Current (A)			Avg. cell voltage (VDC)	Cell weight (kg)	Cell volume (l)
			Average	Peak[a]	Density (A/cm^2)[b]			
Titan TVC	21 × HR58 (36)	36	300	600	0.127/0.254	1.43/1.30	0.87	0.432
ALWT/NUSCAL	157 cell AlAgO Stack	83.3	696	–	1.100	1.32	46.80[c]	24.58[c]
MK67 Mod 1	460 cell MgAgCl stack	50	278	–	1.670	1.087[d]	167.96[c]	77.853[c]
Titan III	20 × 1.8AHP-4	5.5	160	1440	0.30/2.70	1.37/0.30	0.20	0.066
SRAM	19 × 1.3AHP	2.62	17	–	0.093	1.45	0.18	0.023
ADMATT	60 × HR300DC-1	300	325	–	0.059	1.41	3.23	1.259
ADMAT	120 × PML110	110	650	10,000	0.135/2.08	1.36	3.01	1.259
Patriot	39 × 6.0 AHP	6.67	72	168	0.139/0.324	1.33	0.13	0.026
MK53 Mod 1	18 × HR35	35	36	210	0.035/0.202	1.44	0.59	0.265
	60 × HR140DC	140	450	2750	0.100/0.612	1.36	1.70	0.776
GTV Propulsion Battery	HR112(95)DC	110	20	600	0.005/0.133	1.54	1.44	0.664
ATLAS	19 × PMV2(4.5)	4.92	30	2000	0.123/8.24	1.10	0.06	0.038
MK61 Mod 0	236 Mg AgCl bipolar cell stack	30	180	–	0.212	1.11[d]	26.873[c]	12.866[c]
MK46 Mod 1	18 × 22AHP	22	35		0.062	1.42		
	56 × 79AHP	79	450	700	0.138/0.215	1.3	1.20	0.365
UUV	2 × 88 × LR875DC	1100	30	90	0.008/0.023	1.42/1.30	6.56	2.145

Special Test Program

[a] Peak values may not reflect actual specification requirements (i.e., special test/program use).

[b] Avg./Peak, if available.

[c] Battery configuration.

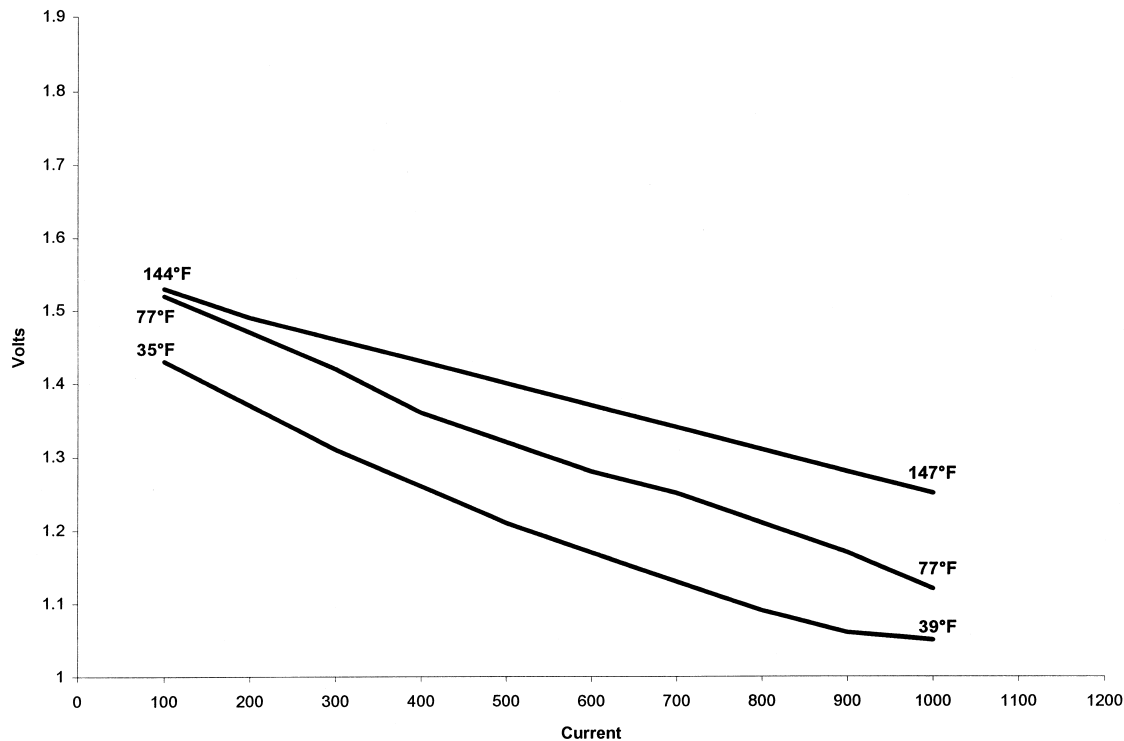[d] Typical battery voltage during discharge is 130 VDC (MK61) and 250 VDC (MK67).

Fig. 1. Polarization data (38% KOH).

for a number of cycles. As a result, the batteries have been designed for operation at higher temperatures. The current-carrying hardware is somewhat heavier and the cell case material has a very high heat deflection temperature (e.g., over 200°C). The LR875DC cell has probably the highest energy density of any rechargeable cell available at a gravimetric energy density of 238 W h/kg and a volumetric energy density of 728 W h/L.
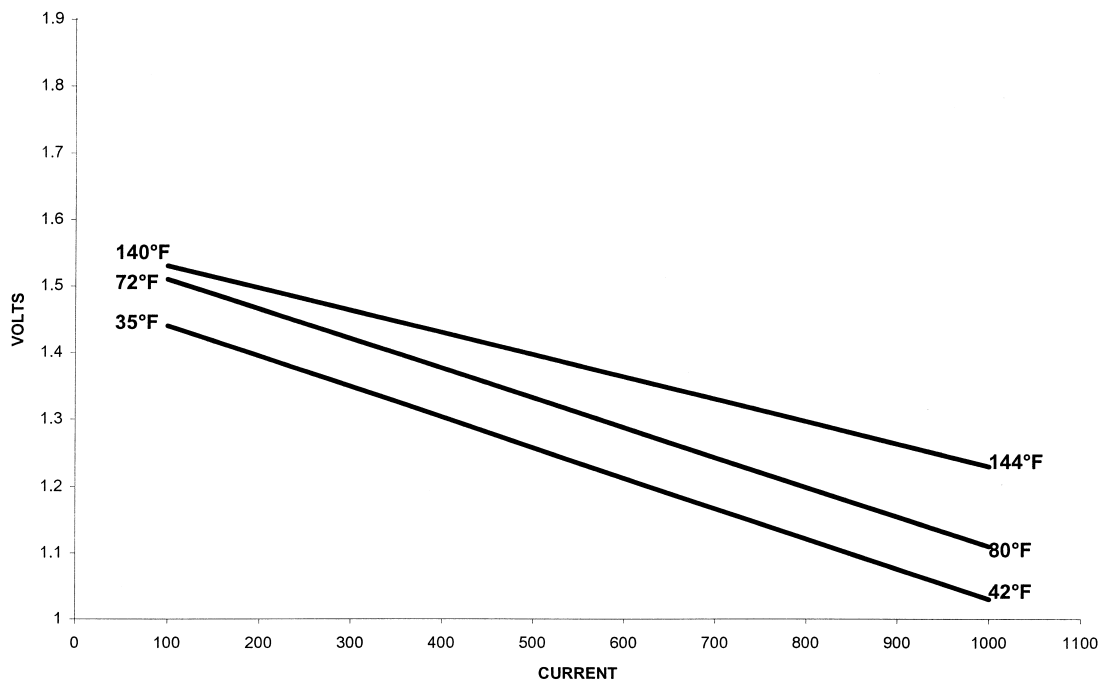

Fig. 2. Polarization data (40% KOH).
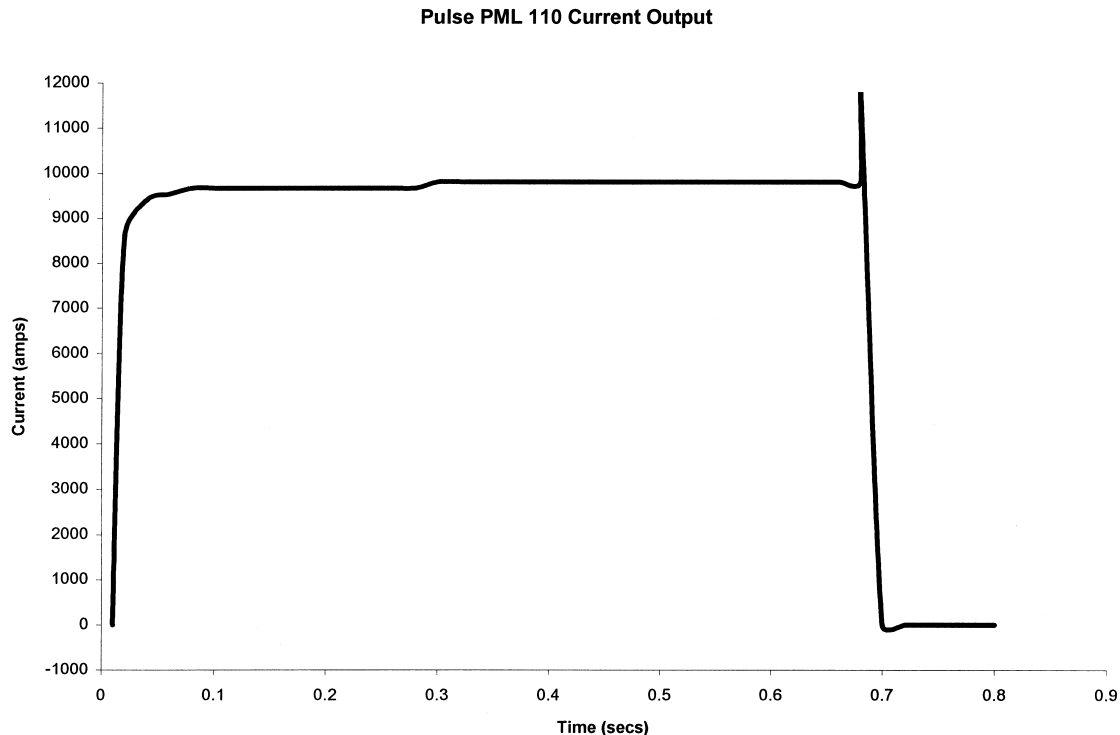
Pulse PML 110 Current Output

Fig. 3. Pulse current output (PML 110).

In addition, silver–zinc batteries, some pressure compensated, have also powered many submarines. For the pressure compensated design, all components are subjected to ambient seawater pressure as the battery and cells are designed to eliminate a pressure differential across their respective enclosure. As a result, all components must be designed to withstand the tremendous compressive stresses that will result from the required operating depths. The discharge rates for the submersible batteries can approach over 1000 A.

2.4. Silver-based couples

These are unique batteries, in most cases, consisting of magnesium–silver chloride, or aluminum–silver oxide used for torpedo propulsion applications. The activation system for standard silver oxide–zinc batteries has been designed to be integral with the battery stack; however, in some cases, activation systems have been mated to the battery cartridge through a disconnect. It is clear that the activation system provides for operational readiness, but exerts a significant penalty on the energy density of reserve, silver oxide–zinc batteries. This has been somewhat compensated by using "pile" construction of circular configuration. This allows the opportunity to utilize the entire cross-section of the shell for active material. Another benefit of this construction is that higher voltage can easily be achieved by increasing the number of cells in the stack and higher current by operating at increased current density without sacrificing volumetric energy density. The electrolyte management system makes provisions for electrolyte flow throughout the cartridge. Due to the higher power capabilities of the aluminum–silver–oxide system, the seawater mixes with caustic flakes or pellets and serves as the electrolyte (i.e., in the form of KOH or NaOH).

For example, the MK61 and MK67 are specifically utilized for high rate torpedo propulsion applications, while the ALWT/NUSCAL design was reviewed as a possible candidate for torpedo propulsion by the US Navy for the lightweight and heavyweight torpedo program [6].

3. Conclusion

For more than 50 years, primary and secondary silver–zinc batteries have attracted a variety of applications due to their high specific energy/energy density, demonstrated reliability, safety, and the highest power output per unit weight and volume of all commercially available batteries. There are a number of other secondary electrochemical systems that someday could provide power densities that are comparable to the silver-based couples such as the lithium-based systems (i.e., lithium-ion). However, none have been developed to the point where they are a direct replacement for the silver–zinc.

References

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