

# Military Applications of Reserve Batteries [and Discussion]

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# Military applications of reserve batteries

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Reserve batteries are batteries which do not give power until activated. They have a long storage life and high power capabilities which makes them useful for numerous military applications. Designs of reserve batteries include those based on movement of electrolyte (sea water, energizers and reserve silver–zinc or lithium–thionyl chloride) and thermal batteries, which are high-temperature batteries activated by heating using an internal pyrotechnic.

The increasing shelf-life of lithium primary batteries and the higher energy density of lithium reserve (particularly thionyl chloride) batteries is allowing these to replace aqueous electrolyte reserve batteries in some applications. Increased energy density of recent thermal batteries makes them more attractive for applications which have previously used other reserve batteries.

## 1. Introduction

In addition to the well-known primary (non-rechargeable) and secondary (rechargeable) batteries, there exist reserve batteries in which the batteries are stored in an inactive state and then are deliberately activated, after which the batteries can supply power, usually for a fairly short time (Linden 1995, ch. 16–22; Attewell 1985). Ordinary primary batteries must satisfy two conflicting requirements: they must be as inactive as possible during storage (to avoid capacity loss) and must be as active as possible during operation (to provide the optimum performance). By using a reserve system, both active and inactive states can be optimized independently, avoiding the inevitable compromise in a primary battery.

The advantages of a reserve design are that reserve batteries can have a very long storage time during which they are inert and therefore the equipment in which they are used is safe against inadvertent activation which is important for military equipment (e.g. mines). Furthermore, some types of reserve battery can produce very high power which is necessary, for example, for missiles or torpedoes. Domestic equipment largely does not share these requirements so reserve batteries are not generally familiar to the consumer market. A domestic example which is effectively a reserve design is the dry-charged lead–acid (car) battery. This is a battery which is complete except that it is not filled with its sulphuric acid electrolyte, so it is inactive with a long storage time. When needed, it is filled with acid and can then be used as a normal battery. Another example is the zinc–air hearing aid battery.

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Table 1. *Battery types*

advantages	disadvantages
primary (non-rechargeable)	
usually low unit cost	cannot be recharged
good performance	expensive if frequently replaced
immediate availability of power	
best for intermittent use	
best for low currents	
secondary (rechargeable)	
fairly low unit cost	low energy density
good performance	capacity loss on storage
immediate availability of power	
cheap if used many times	
reserve (deliberate activation needed)	
very long storage life	expensive
no capacity loss on storage	single use only
highly active chemistry possible	time needed for activation
safe in storage	mechanical complexity
very high power	reliability problems
	lower energy density than primary

On manufacture, the hole which admits the air to the battery is sealed to prevent reaction of the zinc anode by oxidation and capacity loss during storage. For use, the cover is removed and the battery becomes active. These domestic examples differ from military reserve batteries which are used only for short times after activation.

Reserve batteries can be made using most battery chemistries but batteries are normally made with reserve designs only when long storage periods are wanted. In some cases, inadequate storage of primary designs forced the use of reserve ones. Back in the 1920s, the storage life of Leclanche (zinc-carbon, 'dry cell') batteries was very poor, particularly in hot climates, so batteries shipped from Britain to military forces in the Middle East were flat on arrival. The solution was to make the batteries in a reserve format, with water added to form the battery electrolyte immediately before use (Attewell 1989). Nowadays, Leclanche cells have a much better storage life so reserve designs are not needed. A similar problem occurred in the Second World War in the US Pacific Fleet when dry cells for proximity fuses were inadequate. Again the solution was a reserve battery, of the zinc-chromic acid-carbon type (Attewell 1985).

Numerous types of reserve battery have been made over the years (see e.g. Linden 1995). Apart from the batteries of historical interest described above, this review will concentrate on the major types in current or recent production. Future prospects for the different types of reserve battery will be discussed.

Primary, secondary and reserve batteries are compared in table 1.

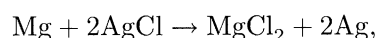
## 2. Design of reserve batteries

In order to make a battery in a reserve format, one component of the battery (usually the electrolyte) must be absent or inactive during storage. Examples already considered are the missing sulphuric acid electrolyte in a dry-charged lead–acid battery, the missing air cathode in the zinc–air battery in its sealed state or the water electrolyte for the reserve Leclanche cell. While one of the essential components of an electrochemical cell (the anode, the cathode or the electrolyte) is missing, the cell is inactive. In some cases, a liquid electrolyte can be added manually (dry-charged lead–acid batteries, reserve Leclanche cells) but this is rarely convenient for military equipment. The electrolyte needs to be added automatically. This is achieved in sea-water batteries simply by immersing the battery in sea water, when the sea flows into the battery, it provides the missing electrolyte (as salt water is a good conductor of electricity) and automatically activates the battery. In other reserve batteries (such as the silver–zinc aircraft emergency reserve battery) a pyrotechnic gas generator is used to drive the liquid electrolyte into the battery to activate it. In the lead–lead dioxide ‘energizers’ (spin-dependent reserve batteries) which are used in shells, the electrolyte is contained in a glass or polythene ampoule. On firing the gun, the shell is fired from the barrel of the gun, the shock breaks the glass ampoule or causes the polythene ampoule to be penetrated, releasing the electrolyte. The spin of the shell caused by the rifling of the gun spins the electrolyte out of the remains of the ampoule and the battery becomes active. In small reserve batteries, such as have been designed to power mines, the electrolyte may be contained in a bellows which, on activation, is compressed either by gas pressure or from a spring, forcing the electrolyte between the electrode plates, and so activating the battery. In all the cases of reserve batteries using electrolyte movement, the skill in the design rests in the mechanical engineering of the electrolyte movement system.

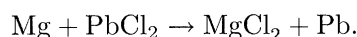
A completely different type of reserve battery is the high-temperature molten salt ‘thermal’ battery which is inactive when cold as the electrolyte is frozen but which is activated by heating to its operating temperature by firing a pyrotechnic which causes the battery to heat up, the salt to melt and become conducting and so activate the battery. All remotely activated reserve batteries require energy input to activate them, either mechanical shock (for gun-launched shells or for mines) or an electrical impulse for a thermal battery.

## 3. Sea-water batteries

Sea water is a convenient electrolyte for batteries which operate in the sea, particularly for reserve batteries, as these can be stored without the weight of the electrolyte and no activation mechanism is needed beyond the removal of a cover over the entry port for the sea water into the battery. As sea water is basically a solution of chlorides, chlorides are used as the cathodes. Magnesium alloy is the normal anode as it is the most reactive metal which can be stored in air without suffering extensive corrosion. The most common cathodes are silver chloride and lead chloride, as these are insoluble in water. The simplified cell reactions are



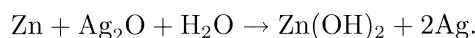
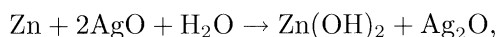
or



The silver chloride system gives the better performance with its higher voltage, lower internal resistance and higher energy density but lead chloride is cheaper and is suitable for low current density applications. Applications for sea-water batteries include emergency lights for life jackets, life rafts and life buoys, power for torpedoes and sonobuoys (Warrell 1979). For life jackets, the reserve nature of the sea-water batteries gives them the advantage that the battery is automatically activated on entry into the sea, so that an emergency light is automatically activated to alert rescue services even if the wearer of the jacket is unconscious. The reserve design makes the battery safe in storage. However, the long lifetime and lower cost of lithium primary batteries is enabling them to replace sea-water batteries for these applications. For light-weight air-launched torpedoes, lithium–thionyl chloride (Danel *et al.* 1986) or thermal batteries (Briscoe *et al.* 1988) are possible future alternatives. For sonobuoys, lithium–sulphur dioxide primary batteries are used in some newer designs because of their higher power. Thermal batteries are also being considered (Slack 1995).

#### 4. Silver–zinc batteries

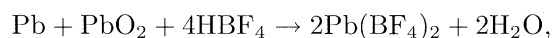
Silver–zinc (Zn–AgO) batteries are used for torpedoes, aircraft emergency power supplies and missiles. The chemistry is described by the equations



They can provide high power and energy density and low-rate designs can operate for many hours. The necessity to store the aqueous potassium hydroxide electrolyte away from the anode and cathode plates and to provide a gas generator to move the electrolyte on activation increase the size and weight of the battery. The mechanical complexity may lead to reliability problems. The silver oxide cathode material has limited storage life, particularly at elevated temperatures (West *et al.* 1986). As with other aqueous electrolyte batteries, low-temperature performance is poor and heaters may be needed. The cost of silver makes these batteries expensive. Thermal batteries have largely replaced them for missile applications and are doing so for aircraft emergency reserve use (Kauffman & Chagnon 1992). Primary lithium–thionyl chloride and thermal batteries may replace them for torpedoes. A lithium–thionyl chloride primary battery was designed to replace a silver–zinc battery of double the weight for an expendable launch vehicle for a space application (Shah 1990).

#### 5. Lead–lead dioxide energizers

These spin-dependent reserve batteries (Linden 1995, ch. 19) illustrate the benefits of a reserve design both to provide long storage life and to provide high power on activation. The electrochemical couple is lead–lead dioxide (Pb–PbO<sub>2</sub>), the same as for the lead–acid battery, but the electrolyte is hydrofluoboric acid (HBF<sub>4</sub>) which leads to soluble reaction products according to the equation



unlike the lead–acid battery where the products for both electrodes are the insoluble lead sulphate (PbSO<sub>4</sub>). This leads to high reaction rates or current densities which would not be possible in a primary battery design as the electrodes would corrode

in the acid. Other electrolytes, such as perchloric acid, have also been considered (Bagshaw 1978).

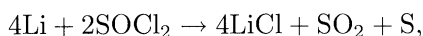
These energizers are used for proximity fuses in gun-launched shells (Casson 1986). Now that long storage lifetimes are possible with lithium primary batteries such as lithium–thionyl chloride (Voorn 1988; Delnick & Baldwin 1990), these may become an alternative power supply in the future for this application. Thermal batteries could also replace Pb–PbO<sub>2</sub> energizers (Briscoe *et al.* 1988).

## 6. Lithium reserve batteries

Lithium batteries are now used for most new applications, particularly in the military, which need high performance. Lithium is the most reactive metal which can be conveniently handled so lithium batteries have higher voltage than aqueous batteries which use less reactive metals such as zinc or lead as the anode. The low equivalent weight of lithium means that only a small weight of lithium is needed in a battery so the energy density is high. Lithium primary batteries are now well established (see, for example, Tuck 1991) and lithium rechargeable batteries are becoming available (Pistoia 1994). Reserve batteries using lithium have also been investigated. The basic principle is similar to aqueous batteries. The battery is stored in an inactive state with the electrolyte stored away from the electrodes. The battery is activated by movement of electrolyte from a reservoir to the space between the plates by various mechanical means, such as springs to compress bellows. Liquid electrolytes and solid cathodes are used for this type of battery. Potential applications include mines. Most modern thermal batteries use lithium (see the following section).

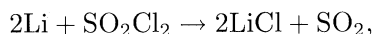
## 7. Lithium–thionyl or sulphuryl chloride reserve batteries

These batteries use the reaction between lithium and thionyl chloride (SOCl<sub>2</sub>) or sulphuryl chloride (SO<sub>2</sub>Cl<sub>2</sub>). The discharge reaction for thionyl chloride is usually described by the equation



but this is doubtless an oversimplification, as both the sulphur dioxide (SO<sub>2</sub>) and sulphur formed can react further with lithium. This chemistry gives a very high energy output, due to the highly reactive nature of the materials. These batteries are widely available in primary format which have long storage time and high energy density (especially at low rates). However, passivation of the lithium can occur, often after long storage at high temperature, which makes the primary batteries unsuitable to supply high power, particularly if discharged at low temperatures. They are used by the military but not to the extent of the cheaper lithium–sulphur dioxide batteries. Civil applications include computer memory back up and gas meters (Saunders 1995).

A related system is the lithium–sulphuryl chloride battery which discharges according to the simplified equation



but this is not as well developed as the thionyl chloride system.

A liquid cathode system, such as thionyl chloride, is ideal for a reserve design as the liquid cathode also serves as the electrolyte solvent. Designs of reserve battery based on movement of the thionyl chloride or sulphuryl chloride have been investigated



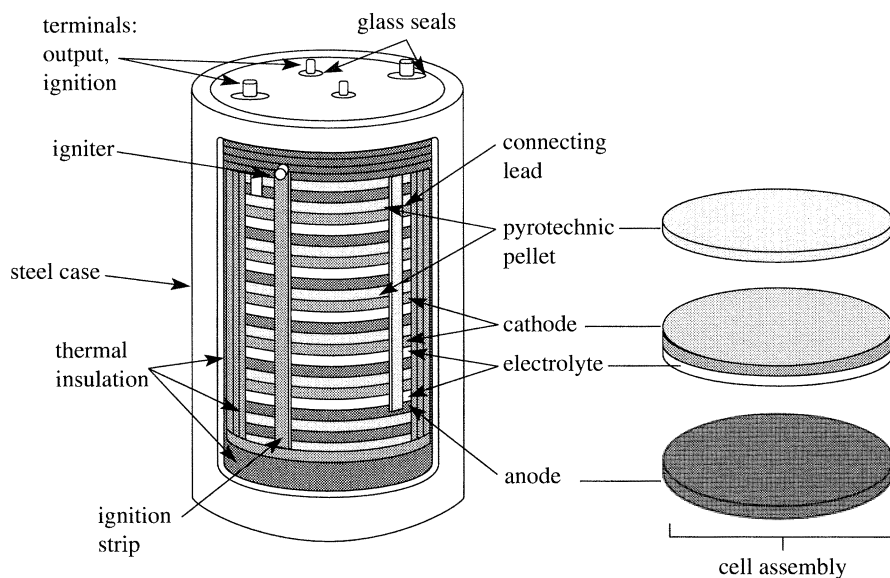


Figure 1. Activation of a thermal battery.

for military applications, such as torpedo propulsion (Chenebault & Planchat 1992). For these applications, very high power and current density are needed and reserve formats are chosen as the battery is inherently safe before activation, there is no change in the electrolyte system during storage, there is no noticeable change in the electrodes during storage and acidic electrolytes can be used which avoids early blocking of the electrodes (Eichinger *et al.* 1990). For a sea buoy, a reserve lithium–thionyl chloride battery was chosen to avoid problems of capacity loss and lithium passivation on storage, which could occur in a primary design, and for improved safety for this very large battery (65 kg) (Remer & Nolting 1992).

The main problem with the lithium–thionyl chloride battery is that the discharge reaction is very energetic and heat management of large size batteries can be difficult. For this reason, thermal modelling of large lithium–thionyl chloride batteries has been necessary (Danel *et al.* 1986). Because of the large quantity of heat released in this reaction, if the reaction became uncontrollable in a large size battery, the consequences could be serious. For this reason, more controllable batteries, such as thermal batteries (see below) may become the future batteries for torpedoes instead of reserve lithium–thionyl chloride.

## 8. Thermal batteries

Unlike the above batteries which require movement of electrolyte to activate them, thermal batteries are activated by melting of the electrolyte which remains in place. There is therefore no need for the battery to have space to store the electrolyte separately in the active and the inactive states, nor is there any need for gas generators etc to move the electrolyte. The design is therefore mechanically simple and reliability is extremely high. Activation of thermal batteries takes place in the following steps (see figure 1).

- (i) An electrical pulse is supplied from an external source to the igniter.
- (ii) The igniter ignites, producing a stream of hot particles which ignite the heat

Table 2. Thermal battery characteristics

advantages	disadvantages
very long storage (over 20 years)	heavy
no maintenance	finite activation time ( <i>ca.</i> 0.1–2 s)
very high reliability	expensive
resistant to shock and vibration	operation time limited ( <i>ca.</i> 1 h max)
high power	high battery case temperatures (up to <i>ca.</i> 300 °C)
wide ambient temperature range	possibly not suitable for high spin

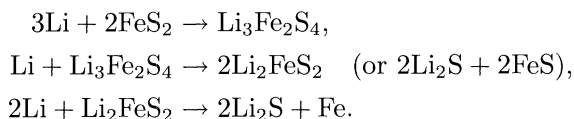
paper, the ‘ignition strip’ in figure 1, which is made of zirconium and barium chromate (Zr–BaCrO<sub>4</sub>).

(iii) The heat paper burns rapidly, igniting the pyrotechnic heat pellets of iron and potassium perchlorate (Fe–KClO<sub>4</sub>) both within the stack and at the end of the cell stack (the ‘end heats’).

(iv) Heat diffuses from the burning heat pellets through the adjacent anode and cathode pellets to melt the electrolyte and to activate the battery.

Thermal battery characteristics are described in table 2.

Modern thermal batteries use the lithium–iron disulphide (Li–FeS<sub>2</sub>) couple, though other chemistries have been used in the past (Linden 1995, ch. 22; Attewell & Clark 1980). The battery discharge is described by the equations



Lithium melts at 180 °C and so, for use in a thermal battery operating at 350–600 °C, it has to be either immobilized on iron powder (the LAN, lithium anode) or it is used as alloys (strictly intermetallic compounds) such as lithium–aluminium or lithium–silicon. The electrolyte is normally lithium chloride–potassium chloride (LiCl–KCl) eutectic, melting at 352 °C. Other salt mixtures, such as lithium fluoride–lithium chloride–lithium bromide (LiF–LiCl–LiBr, melting point 445 °C) have also been considered (Attewell & Clark 1980). In order to keep the electrolyte in place while it is molten, it is immobilized on a binder, such as magnesia (MgO) or silica (SiO<sub>2</sub>). Iron disulphide (FeS<sub>2</sub>) is used as the cathode material as it largely meets the following specifications for thermal battery cathode materials (Ritchie 1993).

- (i) It should have high voltage, to provide high energy density.
- (ii) It must be thermally and physically (dimensionally) stable up to *ca.* 600 °C.
- (iii) It must be indefinitely stable (over 25 years) at storage temperatures (up to *ca.* 70 °C).
- (iv) It should preferably have a stable voltage on discharge, to minimize the need for voltage regulation.
- (v) It should preferably have high electronic conductivity, to allow high power to be drawn.
- (vi) It should preferably have low equivalent weight, leading to high electrochemical capacity.



(vii) It should not form non-conductive discharge products, which increase internal resistance during discharge.

(viii) It should preferably be easily made from readily available, cheap starting materials.

(ix) It should preferably have reasonable thermal conductivity, to allow rapid activation.

(x) The specific heat should be moderate, to minimize the heat input needed from the pyrotechnic.

(xi) It must be chemically stable in contact with the electrolyte, to avoid parasitic chemical reactions.

Iron disulphide has most of these properties but its voltage is only moderate (*ca.* 2.1 V versus Li) and it has only just sufficient thermal stability as it decomposes between *ca.* 500–600 °C (Dallek & Larrick 1988). Hence new cathode materials have been sought (Ritchie 1993) but it is difficult to find materials which meet all the above criteria. Vanadium dioxide (VO<sub>2</sub>) meets most of them but has only moderate electrochemical capacity (Clark *et al.* 1995). It may therefore be suitable for short duration batteries where high energy output is not needed.

A lower melting point electrolyte would be preferable as it would enable faster battery activation and longer battery operation, particularly at low ambient temperatures. Several have been investigated (Redey *et al.* 1990). Recently new electrolytes have been found which combine high electrical (ionic) conductivity with low melting points (Ritchie 1995).

One disadvantage of thermal batteries is that they are heavy for their size. A major component of the weight is the weight of the stainless steel case. Lighter metals, such as titanium, could reduce this (Embrey *et al.* 1992).

The major application for thermal batteries is missiles though they are being tested for aircraft emergency reserve applications (Kauffman & Chagnon 1992). They may find applications in sonobuoys (Slack 1995). Recent developments, leading to higher energy density, make thermal batteries more attractive for underwater applications (Clark & McKirdy 1993). Improvements are probably needed in stability under high-spin conditions before they could be used in gun-launched weapons.

## 9. Conclusion and future for reserve batteries

Reserve batteries are needed whenever power supplies with long storage time without maintenance are wanted. This particularly applies to military applications. Reserve batteries are inert during storage which improves safety. Some types supply high power, needed in some military applications.

Because reserve batteries are used for many military applications, they are largely dependent on the military market. With worldwide cuts in military expenditure, this has led to a reduction in demand for reserve batteries. Changes are taking place within the reserve battery market. Smaller reserve batteries (such as sea-water batteries for life jackets etc or lithium reserve batteries for mines) are subject to competition from lithium primary batteries, such as lithium–thionyl chloride. For sonobuoys, sea-water batteries are being replaced by lithium–sulphur dioxide primary batteries and thermal batteries may be used in future. Silver–zinc batteries have largely been replaced by thermal batteries for missile applications and may be replaced by thermal batteries for aircraft emergency reserve. For torpedoes, silver–zinc could in future be replaced by reserve lithium–thionyl chloride or thermal batteries. Energizers for

proximity fuses in shells could be replaced by reserve lithium–thionyl chloride. The general trends are for reserve aqueous batteries to be replaced either by primary or reserve lithium batteries or by thermal batteries.

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### Discussion

N. E. BAGSHAW (*Consultant, Stockport, UK*). Dr Ritchie mentioned the possible replacement of sea-water batteries for torpedoes by thermal batteries. The present sea-water battery has, I think, a volumetric energy density of  $300 \text{ Wh l}^{-1}$  at the 6 min rate. This is a formidable target to beat. What is the projected energy density of the thermal battery for this application?

A. G. RITCHIE (*DRA, Farnborough, UK*). Considerable work has been done recently on the development of large size thermal batteries (see Clark & McKirdy 1993). Individual thermal battery cells (including pyrotechnic) achieved  $150 \text{ Wh kg}^{-1}$ ,  $400 \text{ Wh l}^{-1}$ , complete batteries achieved  $80\text{--}90 \text{ Wh kg}^{-1}$ ,  $230\text{--}260 \text{ Wh l}^{-1}$ . Projections for larger batteries were  $110\text{--}120 \text{ Wh kg}^{-1}$ ,  $310\text{--}330 \text{ Wh l}^{-1}$ . Energy densities for thermal batteries are therefore at least comparable with the  $300 \text{ Wh l}^{-1}$  for a sea-water battery quoted by N. Bagshaw.