

THE BEHAVIOUR OF LITHIUM BATTERIES IN A FIRE

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Summary

Fire trials are described that involved all of the types of lithium primary cells commercially available in the U.K. and of interest for Defence applications. The electrochemical system and the design of the cell case caused major differences in behaviour. These are discussed, and hazards to personnel evaluated. The efficacy of a water spray as an extinguishant is emphasised.

Introduction

Lithium primary batteries are becoming increasingly deployed by the U.K. Armed Services. The majority is of the sulphur dioxide type, but copper oxide, manganese dioxide and, to a limited extent, thionyl chloride designs are in use. Most use cylindrical cells in the capacity range 0.5 - 35 A h.

With large stocks of batteries in depots and Unit stores, advice on storage conditions and fire-fighting methods was sought.

This paper presents some of the work done at the Royal Aircraft Establishment to determine the consequences of a fire spreading to stocks of lithium batteries, and the efficacy of water as an extinguishant.

Flammability of lithium batteries

All lithium cells contain flammable material. Lithium is the substance which, understandably, emphasises the fire hazard of these cells, but all except the oxyhalide systems contain a flammable liquid as, or part of, the electrolyte system. Relevant characteristics of some commonly used organic fluids are given below, together with the cathodes with which they are usually associated.

Earlier work [1] showed that small amounts of burning lithium could be extinguished by using a spray of water. It was also found that, in a fire involving SO₂ batteries, jetting flames fuelled by acetonitrile escaping from cell vents would present the major fire hazard [2].

	Cathode	Flash point (°C)	Boiling point (°C)
Dioxolane	CuO	+2	78
Acetonitrile	SO ₂	10	80
Dimethoxyethane (DME)	MnO ₂	30	83
Butyrolactone	(CF) <i>n</i>	98	206
Propylene carbonate (PC)	SO ₂	120	242

Unpublished work indicated that components of lithium cells could be expelled many metres from a fire and it was known that SOCl₂ cells would rupture violently if they did not have an adequate vent.

These factors were considered when planning the trials.

The batteries

A considerable quantity of surplus batteries, mostly undischarged single cells, were used, and they represented all of the chemical systems and designs available in the U.K. that are, or are likely to be, in use for defence applications.

Thus lithium-SO₂, MnO₂, (CF)*n* and various oxyhalide systems in the spiral-wound format, plus MnO₂ and SOCl₂ cells of bobbin construction were all tested.

Individual cells in the R20 ('D'), R14 ('C') and R6 ('AA') sizes predominated, but several multi-cell batteries were included.

In these trials, fibreboard boxes, each 230 mm × 180 mm × 180 mm high were used to hold individual cells. One box held about sixty of the R20 size. To prevent the cells from spilling out as soon as the fibreboard had burnt, they were held in the boxes by a small amount of polyester resin.

Different cell systems and manufacturers' types were in separate boxes.

The site

For the hearth, a stout sheet of expanded steel sheet, 800 mm × 600 mm, was supported on building blocks to a height of 900 mm. A sprinkler head was located 1.5 m above the hearth. When required, it was supplied with water from a fire tender at 90 l min⁻¹. Fuel for the initial fire was wood. Up to eight boxes were placed on the hearth and burnt in each trial.

In some trials, cell components were prevented from leaving the hearth by a cage of expanded steel mesh placed over the boxes.

During the trials, the weather was dry, with a 5 - 10 knot (2.5 - 5 m s⁻¹) wind blowing across the site.

Dry grass and heather surrounded the test area. Two video cameras recorded events, being placed 100 m away and at right angles to each other. Marker posts, 2.5 m high and 2 m apart, were in line with the cameras.

Figures 1 and 2 show the hearth and site.



Fig. 1. General view of test site.



Fig. 2. Hearth and sprinkler system.

Typical results

(i) Without fire fighting

Cell type etc.	Time (min) to:		Observations
	1st event	last event	
CuO. 4 boxes R6 size cells. Grommet seals	3	9	Very fierce fire. Cell cases projected 60 m from site. Unburnt lithium found several metres downwind.
SO ₂ . 4 boxes R20 size cells. Hermetically sealed with base vent.	3	14	Burning on hearth. Cells 'jet propelled' from site to 12 m. Still burning on impact. Small grass fires. Most cells entire but a few cases split open. In cells projected from fire, lithium generally unburnt.
SO ₂ . 4 boxes R20 size cells. Side vent design.	3	15	Burning on hearth. Few cells left site. No cell cases split open.

(continued)

(continued)

Cell type etc.	Time (min) to:		Observations
	1st event	last event	
SO ₂ battery. Twenty R20 cells. Side vents. Partly potted.	5	12	Gentle venting. Flaming from vents. Cells stayed on hearth.
MnO ₂ spiral wound. Aluminium cases. 2 boxes, various cell sizes.	2	8	Fierce fire. No projection of cells or components beyond fire site. All cell cases melted.
MnO ₂ spiral wound steel cases. Grommet seal. 2 boxes, various small sizes.	2	7	Fierce solvent fire. Cell components, including unburnt lithium, a few metres downwind.
MnO ₂ bobbin type. 2 boxes.	3	8	Fierce fire. Most of lithium unburnt, being projected a few metres downwind.
(CF) <i>n</i> spiral wound. R14 size. 2 boxes.	4	10	Fierce solvent fire. Less intense than MnO ₂ but longer. No projections.
SOCl ₂ bobbin type. Steel case. No vent. 1 box. Various sizes to 'DD'.	4	8	Explosions — 'small arms fire'. Cases to shrapnel, found 20 m from site. No fire. Dense white smoke, HCl and Cl ₂ smell. Unburnt lithium 2 m away.
SOCl ₂ spiral wound. Steel case, base vent (SO ₂ type). 1 box. Various sizes.	3	8	As above. Cases ruptured. Components of spiral projected. Unburnt.
SOCl ₂ bobbin type. Side vent. R6 size.	3	7	Much quieter. Generally vent opened and case did not fragment.
SOCl ₂ pancake design. Various sizes.	3	6	Gentle venting. Pressure released through terminal seals.
SO ₂ Cl ₂ spiral wound. Steel cases. No vent. Various sizes, to 'D'.			Explosions louder than SOCl ₂ spiral. Otherwise similar, but parts 40 m away.

(ii) Without fire fighting. Boxes covered by mesh cage

The steel mesh cage effectively prevented any cells or their components from leaving the fire site. Generally, the timing and nature of other events were the same. In the previous trial, with the boxes uncovered, little signs of lithium burning on the hearth were apparent, but in these tests the characteristic carmine colour of the burning metal could be seen some 2 - 5 min after the solvent fires started.

(iii) Effect of water spray

The sprinkler was started once the cells were burning fiercely or were venting. Passing about 90 l min^{-1} , the rate of water delivery onto the hearth was about $10 \text{ l min}^{-1} \text{ sq metre}^{-1}$.

Apart from oxy-halide batteries, the fire was killed within 20 s. With oxyhalide batteries, the rate of cooling was such that the rupturing of cells stopped in a similar time.

After the fires, many of the cells both on, or away from, the hearth were found to contain unburnt, resolidified lithium.

Problems after a fire

In the context of this investigation, it is likely that after a fire has been successfully extinguished by water, a number of very wet, but unburnt, batteries will remain. It is good packaging practice to seal lithium batteries individually within plastics envelopes. Should these still be intact, and the batteries therefore dry, there should be no hazard. However, if the plastics wrappings have melted, or none was present, then wet lithium batteries, perhaps standing in water, may be hazardous.

Perforation of exposed cell cases can occur from electrolytic action. The time that this will take is dependent upon the ambient temperature, the area of case exposed, but mainly upon the conductivity of the water (fresh or saline), and on the driving potential (number of cells in series).

For example, a battery containing ten, series connected, partly potted, sulphur dioxide cells of R20 size was partly immersed in water at 20°C . To promote electrolytic corrosion at the case (negative terminal) of the most positive cell in the chain, part of its insulating plastics sleeve was removed.

After immersion in ordinary tap water for 1 h, little attack had occurred although ionic conductivity was increasing, as shown by the blue colouration of the water from dissolved Cu species (from connecting wires) and by an increase in gassing.

Immersion in a 3.5% saline solution caused vigorous activity. There was a high gas evolution from the cell case, water temperature rose, and within 15 min the case had perforated. Sulphur dioxide was released and hydrogen evolution increased as the lithium within the cell reacted with the water. This latter action was gentle, and in this experiment presented no hazard other than that associated with the generation of hydrogen.

Conclusions

(i) Under warehouse conditions, the major contributor to a lithium battery fire is, when present, the flammable electrolyte. Lithium metal itself makes only a minor contribution.

(ii) Copious application of water, as a spray, is an effective extinguisher for burning batteries or individual cells, irrespective of their type.

(iii) In a fire fed by wood and card, it will take several minutes for the individual cells in a bulk stock of packaged batteries to react to the fire.

(iv) The objective should be to extinguish the fire by the quickest method available. The residue will contain cells in a variety of conditions.

(v) Several cell systems react violently in a fire. The explosive rupturing of the cases of oxyhalide cells and the projection of fragments will be a hazard to fire-fighters. Effective, low-pressure vents in all such cells is advocated. The nature of the vent in the SO_2 system affects its behaviour.

(vi) Of solid cathode systems, the CuO type with dioxolane electrolyte behaves spectacularly, projecting empty cell cases tens of metres from the fire.

(vii) The other solid cathode types, MnO_2 and $(\text{CF})_n$, behave benignly. Little is expelled from the fire site and, although the solvent fires are fierce, they would present no special problems to firefighters.

(viii) Wet batteries may present a minor hazard for several hours after a fire has been extinguished.

References

- 1 A. Attewell, in J. Thompson (ed.), *Power Sources 9*, Academic Press, 1983, p. 473.
- 2 M. C. Puttock, in J. Thompson (ed.), *Power Sources 9*, Academic Press, 1983, p. 527.