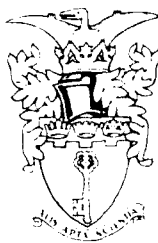


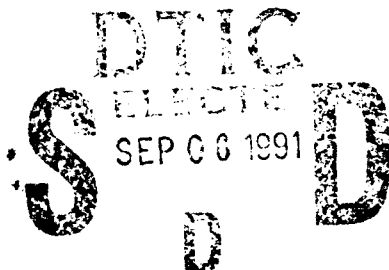
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by

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TEMPERATURE CONTROL IN THERMAL BATTERIES
(TERMOSTATIROVANIE TEPLOVYKH BATAREI)

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EDITOR'S SUMMARY

Methods of temperature control in thermal batteries are described. Different insulating materials are reviewed and the use of metal wraps round the cell stack to act as heat sinks is described. Salt mixtures which undergo phase changes at the operating temperatures of thermal batteries can be used as heat stores. Pyrotechnics with different burning speeds can be chosen to control the rate of heating of thermal batteries.

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Temperature control in thermal batteries, whose operation depends on the melting of an electrolyte by means of pyrotechnic heating, is provided in order to maintain the temperature of the electrochemical elements (EKHE) within the required working range of 350-700°C¹.

Existing methods of temperature control in thermal batteries are classified as active and passive. Passive temperature control provides thermal stability of the EKHE mass by placing around it layers of thermal insulating material. Active temperature control provides for the introduction of heat into the element block from one or another source arranged inside the battery, and for it to be effective over the working period.

Thermal insulating layers are commonly achieved by means of materials of low heat conduction which must exhibit chemical stability against molten salts, withstand short-term temperature rise, and be mechanically stable against shock and centrifugal loads.

In thermal batteries tough, resilient thermal insulators are employed. Kaolin-based fabric, fibreglass and asbestos² are used in such materials. The element block may be wrapped in them; it is also possible to have alternate layers of various materials, for example, ceramic, glass fibre or mica³.

Tough thermal insulation is achieved by the use of thermally stable ceramic. The element block is placed in ceramic enclosures made from oxides of silicon, aluminium, titanium and other materials^{2,4-6}. The most effective thermal insulator is a material known as Min K-2002, obtained by compression of 75% by weight of pyrogenic silica, 9% quartz fibre and 16% titanium dioxide⁷. The thermal conductivity of this material at a density γ of 0.32 to 0.37 g/cm³ is $\lambda = 6.9$ to 9.6×10^{-5} cal/cm.s.°C in the temperature range 260-650°C.

The gases formed by the combustion of the heat generator when the thermal battery is initiated have a strong influence upon the process of thermal transmission in passive thermal insulators. Hydrogen, for example, penetrating the pores of the insulator doubles the rate of thermal loss^{8,9}. In order to exclude the effect of gases on the transfer of heat and prevent their penetration into the pores of the thermal insulating material, non-permeable gas barriers are established between the latter and the element block⁸⁻¹¹. Sometimes an inert gas having a thermal conductivity less than that of air is introduced into the pores of the thermal insulating material (Table 1).

Table 1

Thermal conductivity of fibreglass in atmospheres
of various gases at 190°C⁹

Gas	Thermal conductivity $\lambda \cdot 10^4$ cal/cm.s.°C
Helium	4.34
Nitrogen	1.30
Argon	0.996
Krypton	0.717
Xenon	0.565
Vacuum (0.02 mm Hg)	0.237

All types of active thermal insulation may be divided into three groups: temperature control by the thermal capacity of heated layers, by heat-storing materials and by exothermic reactions occurring during the operation of the thermal battery.

As an example of the first group^{12,13}, a sheet of stainless steel, copper or other metal is placed around the sides of the EKHE block; the use of this prolongs the working of the thermal battery on account of the increase in its thermal capacity and the improved conditions for temperature regulation. To achieve these aims a combination of metal sheets and heat-storing pellets⁷ placed around the EKHE block are employed. However, more effective temperature control is obtained using heat-storing materials (Table 2), which are characterised by a high specific heat of fusion and a phase change within the working temperature range of the thermal battery.

Table 2

Substances melting in the temperature range 400-500°C⁹

Substance	T_{PL} , °C	Heat of fusion cal/cm ³	Thermal capacity in solid state cal/cm ³ °C	Thermal conductivity $\lambda \cdot 10^4$ cal/cm.s.°C
PbCl ₂	483 (498*)	121	0.398	15
CdSb	456	216	0.378	52
Te	438 (450*)	204	0.338	50
TlCl	427	215 (115*)	0.379	20
Zn	420	198	0.705	2701

* values in Ref 9 - translator's note

On activation of the thermal battery the heat-storing substances obtain thermal energy from the combustion of the pyrotechnic heat generator, and after

receiving a certain amount they undergo a phase change with an absorption of heat. When the thermal battery cools and the heat-storing substances reach the temperature of crystallisation, heat is given out, counteracting the thermal losses and maintaining the EKHE block in its working condition. The use of heat-storing materials in thermal batteries causes undesirably high temperatures in the EKHE block to be reduced, as a result of their absorption of the surplus thermal energy given out during the combustion of the pyrotechnic heat generator.

Binary eutectics of salts melting in the range 450-500°C (Tables 3 and 4) are usefully employed as heat-storing materials, the best being the eutectics $\text{Li}_2\text{SO}_4\text{-NaCl}$ and LiF-KF , since they possess a high heat of fusion - 94.1 and 111 cal/g respectively. Also in use are eutectics of the salts $\text{CaCl}_2\text{-NaCl}$ ($T_{\text{PL}} = 505^\circ\text{C}$) and LiCl-NaCl ($T_{\text{PL}} = 552^\circ\text{C}$)^{15,16}, the ternary systems of salt eutectics¹⁴, eutectics of the metals CuSb ($T_{\text{PL}} = 526^\circ\text{C}$), CdSb ($T_{\text{PL}} = 456^\circ\text{C}$) and metals which readily melt such as zinc^{9,13}.

To prevent running away on melting the salt composition is thickened with finely divided powder. For example a powder of eutectic composition $\text{Li}_2\text{SO}_4\text{-NaCl}$ is mixed⁷ with a finely divided powder of silicon dioxide (200 m²/g) in the proportions 85:15. The pellets obtained under pressure have a density of 1.7 to 1.8 g/cm³ ^{17,18}. The readily molten metals used as stores of heat are placed in metallic layers and shaped^{9,13}.

Table 3

Binary eutectics of salts melting within the working temperature range of the EKHE⁷

Melting temperature of eutectic °C	System A-B	Composition	
		Component A mol. %	Component B mass %
450	$\text{MgCl}_2\text{-NaCl}$	40.0	52.0
470	KCl-MgCl_2	48.5	42.5
481	$\text{LiCl-Li}_2\text{SO}_4$	64.0	41.0
499	$\text{Li}_2\text{SO}_4\text{-NaCl}$	58.7	72.6
507	$\text{LiCl-Li}_2\text{CO}_3$	61.0	47.0
522	$\text{KCl-Na}_2\text{SO}_4$	59.0	43.0
530	$\text{Li}_2\text{SO}_4\text{-Li}_2\text{CO}_3$	60.5	69.5
535	$\text{K}_2\text{SO}_4\text{-Li}_2\text{SO}_4$	20.0	28.0
544	$\text{K}_2\text{CrO}_4\text{-Li}_2\text{CrO}_4$	54.0	64.0
550	$\text{KBr-Na}_2\text{SO}_4$	43.7	39.4

In practice, heat stores may be placed both around the sides and in the centre of the element block. In certain designs a combination is possible in which heat-storing salt pellets are placed in the centre of the element block, and heat-storing sheets made, for example, from steel are located around the sides^{15,16}. Also, heat-storing materials may be placed around the perimeter of the EKhe block^{15,16,19,20}. At Ref 20 there is an application of a design of battery having a case in two layers. Between the sides of the case is situated a material which passes from the solid to the liquid phase when the temperature of the sides of the case of the thermal battery increases. When the heat-storing substance hardens, heat is given off, and maintains the required working temperature of the EKhe block, although the battery may be in a cold environment. In this battery, the heating and melting of the heat-storing substance, for example, naphthalene, is due to pyrotechnic or electric heating, built into the sides of the case.

Table 4

Two-component salt systems having melting temperatures within the working range of the EKhe¹⁴

Melting temperature of eutectic °C	System A-B	Component A mol. %
453	LiBr-LiF	70
460	LiF-RbF	45
485	LiCl-LiF	71
487	LiCl-SrCl ₂	65
492	LiF-KF	52
493	CsCl-NaCl	65
510	BaCl ₂ -LiCl	37
544	KF-KI	32
546	NaCl-RbCl	46

The third method of active temperature control is by means of exothermic reactions which proceed during operation of the thermal battery; this is described at^{9,13,21,22}. By placing pyrotechnic layers in the sides of the case and igniting them via a touch-hole, the time for which the EKhe block can be held in an active condition can be doubled²². The EKhe block is surrounded by thermal insulation using asbestos fibre.

For a source of heat it is possible to employ a radioactive isotope contained in a sealed capsule inserted in the ignition channel of the battery²³. The upper part of the capsule projects beyond the end of the ignition channel. During storage of the battery, the ampoule containing the isotope is held in the

upper part of the capsule by a wire in contact with the pyrotechnic heat generator. On activating the battery the wire burns through, and the ampoule with the isotope moves under the influence of a spring into the working position. The heat given out by the decay of the radioactive isotope reduces the rate of cooling of the EKHE block. For example, a battery of normal construction having a diameter of 5 cm and a height of 4.5 cm can supply a current of 0.1 A at 10 V over a period of 4-5 minutes. The same battery provided with 6 cm³ of Sr⁹⁰TiO₄, will have its useful capacity increased 20 times, with a working period of approximately 90 minutes. The strength of radiation in the stated quantity of isotope amounts to about 2 rad/h. It is possible to use other isotopes, for example Pu²³⁹ or Cm²⁴⁴ ²³.

In order to maintain the thermal operating conditions of the battery, exothermic effects due to a combination of fast and slow burning pyrotechnic compositions may be employed. For example, a slow burning mixture was made by preparing 1 mm thick pellets¹⁹ from 25-45 g BaO₂ (particle size up to 10 μm), 25-45 g Sb₂O₃ (particle size up to 5 μm), 8-15 g CuO (particle size up to 5 μm), 10-40 g SnO₂ (particle size up to 5 μm). One gram of such a mixture burned for 0.5 to 10 hours. A fast burning mixture was prepared from 55-80 g Pb₃O₄ (90% of particles up to 10 μm), 20-45 g Si or FeSi (50% of particles up to 7 μm). One gram of this mixture burned for 0.5 second. A slow exothermic reaction is achieved by having in the pyrotechnic heat generator 70% of the fast and 30% of the slow burning mixture.

A method described at^{9,13,21} is of interest: a number of metals which give off heat on alloying may be employed as stores of heat. For example an exothermally alloying mixture of lithium and lead-tin solder (40% Pb and 60% Sn by weight) gives off 230 cal/g. To protect the lithium from damp and oxidation, and also to prevent the running away of molten metal during the operating period of the thermal battery, they are rolled into metallic cup-shaped shells^{9,13}.

There are a variety of designs related to the third group of active temperature control; there are batteries²⁴ in which the pyrotechnic heat generator is situated in the insulation, which is placed around the perimeter of the EKHE block. To achieve the maximum effect the rate of combustion of the pyrotechnic heat generator placed in this way may be lower than that of the basic types²⁵. In certain designs the EKHE block surrounds a layer of pyrotechnic paper, which is ignited via separate touch-holes⁶.

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