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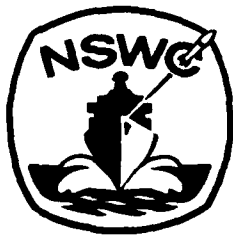
THE RELATION OF BATTERIES TO EXPLOSIVES

BY CAROL FREEMAN

RESEARCH AND TECHNOLOGY DEPARTMENT

SEPTEMBER 1980

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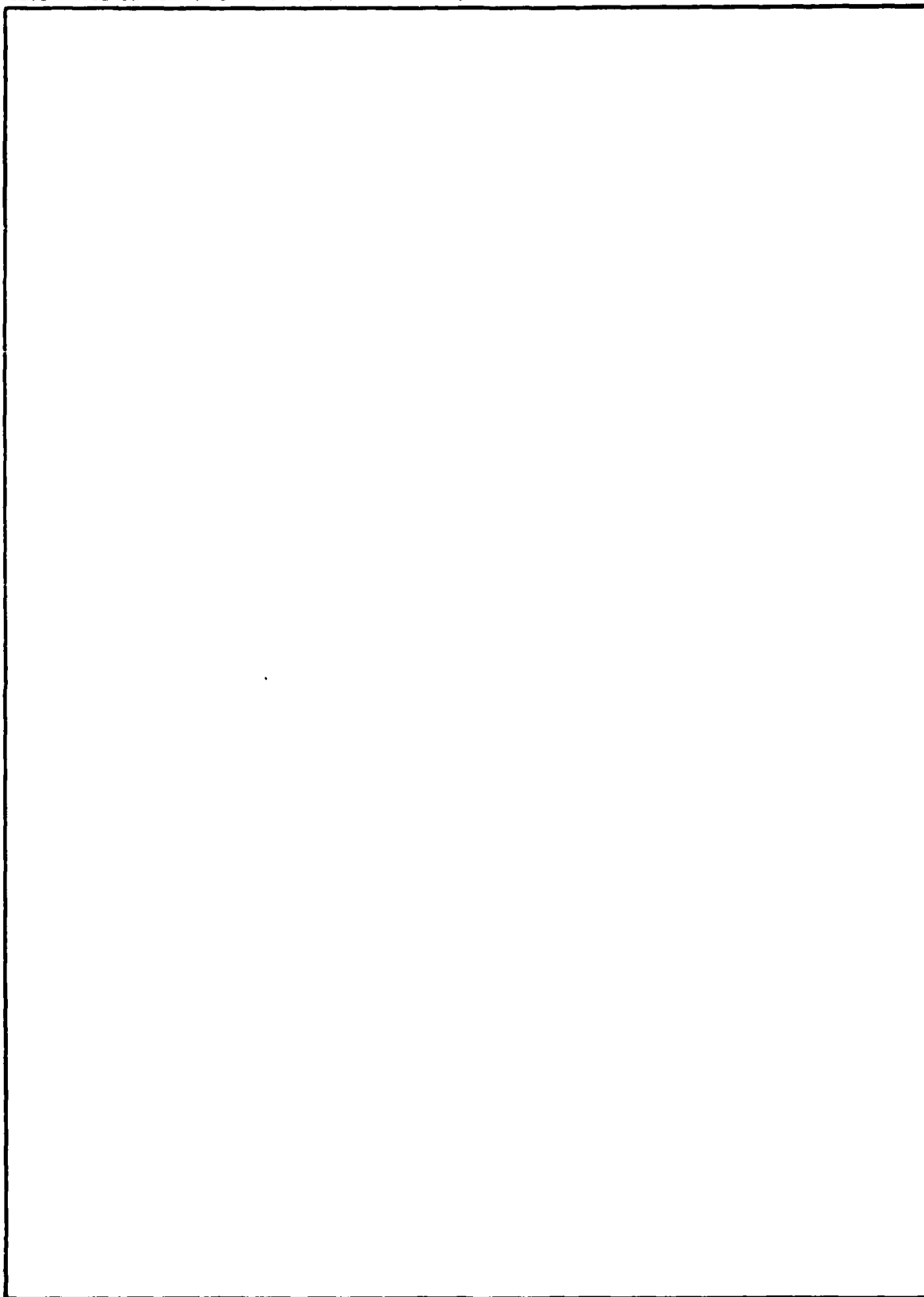
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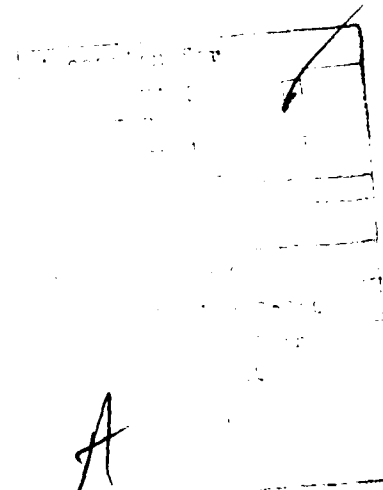
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CHAPTER 1

INTRODUCTION

It is important to view all batteries as potential explosives. In order to discuss the relationship of various electrochemical systems to explosives, one must first discuss some of the more common explosives terminology. This paper defines explosives terms and relates them to batteries.

CHAPTER 2

EXPLOSIVES

An explosive is defined as any substance or mixture of substances in a metastable state which will, with suitable stimulus, undergo rapid chemical change into more stable products, largely gaseous, that have a much lower energy than the reactants. The energy released during the reaction is primarily heat. If the conversion of reactants to hot gaseous products is very rapid, the reaction essentially occurs at constant volume and extreme pressures develop. Once generated, subsequent expansion of the hot gas is the destructive force of the chemical explosion.

Explosives are divided into three categories, according to the rate at which the chemical reactions (gas expansion) proceed: deflagrating, detonating, and thermal explosives. Descriptions of these three categories are given in the following paragraphs and are derived from references 1 through 7.

DEFLAGRATING OR LOW ORDER EXPLOSIVES

A deflagrating, or low order explosive, is an energetic material which undergoes rapid combustion after being initiated by a spark or flame. The chemical energy released from the reaction zone is transmitted to other layers of unburnt material by heat transfer. The reaction zone is defined as the region in which reactants are converted to products. In the reaction of a deflagrating explosive (a deflagration), the reaction zone propagates at a velocity (several centimeters per second) less than the local velocity of sound. Because the rate of propagation is low, no shock waves are generated in the deflagration reaction.

¹Cook, M., The Science of High Explosives (New York: Reinhold Publishing Corp., 1958), pp. 1-4, 172-175.

²Meyer, R., Explosives (New York: Weinheim, 1977), pp. 58, 61-65, 72, 107-110.

³Gregory, C. E., Explosives for North American Engineers (Cleveland: Technical Publishing Co., 1973), pp. 19, 27-33, 67, 262, 264.

⁴Private communication with J. Pastine

⁵Private communication with Larry E. DeVries

⁶Private communication with Benjamin Larrick

⁷Macek, A. "Sensitivity of Explosives", Chemical Reviews, Vol. 62, No. 1, 1962, p. 41.

DETONATING OR HIGH ORDER EXPLOSIVES

A detonating, or high explosive, is an energetic material which undergoes a rapid, self-sustaining chemical reaction. The chemical energy released from the reaction zone is transmitted to the unreacted material via shock waves. In a detonation, only a tiny portion of the liberated energy is transmitted by heat transfer. The detonating explosive has extremely high rates of energetic chemical reaction and evolves great pressure relative to the deflagration reaction. In the reaction of a detonating explosive (a detonation), the reaction zone propagates at a velocity greater than the local velocity of sound. Since the pressure in a detonation is thousands of atmospheres, and the resulting gas density is very high, the local velocity of sound may be as high as several kilometers per second. The reaction time (time of conversion of reactants to products) is in microseconds.

Detonating explosives are subdivided into three classes: primary, secondary, and booster explosives. This subdivision is based upon how easily the explosive detonation reaction may be initiated. This ease of initiation is termed sensitivity. The more sensitive an explosive, the less energy is required to initiate its explosive reaction.

PRIMARY EXPLOSIVES. Primary explosives are the most sensitive class of high explosives. They are usually inorganic salts such as lead azide, PbN_3 . A primary explosive is initiated by a primary heat source such as flame, spark, hot wire, or heat produced by impact. Following initiation, the primary explosive develops detonation in two stages. The first stage is deflagration. As the deflagration reaction progresses, it generates pressure. The rate of the deflagration reaction, being a function of pressure, increases as pressure increases, until there is a sudden transition from deflagration to detonation. Primary explosives are used in electric or mechanical primers as initiators for fuze explosive trains.

SECONDARY EXPLOSIVES. Secondary explosives are generally the least sensitive class of detonating explosives. Their initiation usually requires detonation via a shock wave generated by detonating a primary explosive. The shock wave heats and compresses the secondary explosive. This initiates a chemical reaction of the explosive in the region of the shock. If this chemical reaction attains a rate greater than a defined value, specific to the particular explosive, the energy released in the reaction reinforces the shock wave. The result is detonation.

For safety reasons, the secondary explosive comprises a large portion of the main explosive charge in most military and commercial uses because of its relative insensitivity.

BOOSTER EXPLOSIVES. Frequently a secondary explosive is so insensitive that it requires a booster to aid in detonation. Booster explosives are a class of detonating explosives, moderately sensitive, which are detonated by a primary explosive. The booster charge creates a shock wave which strengthens the detonation wave of the primary charge, creating a very powerful shock wave which detonates the main charge (secondary explosive).

THERMAL EXPLOSIVES

A thermal explosion is initiated by a self-heating reaction in which a portion of the explosive is heated, thus initiating energetic chemical reactions. These energetic reactions liberate heat, which further elevates the temperature of the system. The increase in temperature increases the kinetics of the exothermic reactions, which in turn further heats the system. This cyclical phenomenon is called thermal runaway. Thermal explosion occurs when the rate of energetic chemical reaction increases exponentially to that of deflagration or detonation.

CHAPTER 3

EXPLOSIVE REACTIONS

Now that the three major categories of explosives have been discussed, it is important to discuss explosive reactions in terms of the enclosure in which the energetic material is contained. This is necessary because batteries are made up of contained energetic materials.

Military Standard #1648 (AS) defines five types of explosive reactions in terms of the enclosure in which the energetic material is contained. In order of increasing severity they are: burning reaction, deflagration reaction, explosion, partial detonation, and detonation.

BURNING REACTION

In a simple burning reaction, the energetic material undergoes a simple combustion which may open up or vent the container. The container will remain in place but may collapse due to structural failure. In a burning reaction, there is a minimal damage to the environment.

DEFLAGRATION REACTION

In a deflagration reaction, the energetic material undergoes rapid combustion which ruptures the enclosure. The container or major parts of the container may be thrown up to 50 feet by the reaction. In a deflagration reaction, there is no damage due to blast or fragmentation effects.

EXPLOSION

In an explosion, the energetic chemical reaction causes violent pressure rupture of the container. There is fragmentation of the container into large pieces. An explosion produces minimal air shock. There is some blast and fragmentation damage to the environment.

PARTIAL DETONATION

In a partial detonation, only a portion of the total energetic material detonates. There is fragmentation of the container into small and large pieces. A partial detonation produces strong air shock. There is extensive blast and fragmentation damage to the environment.

DETONATION

A full detonation produces fragmentation of the container into tiny pieces. It produces maximum possible air shock. In a detonation, there is maximum blast and fragmentation damage to the environment.

CHAPTER 4

BATTERIES

Under severe conditions, almost any battery can be forced to explode. Most batteries contain energetic chemical materials, which, under the appropriate physical conditions, can become metastable with respect to spontaneous, energy-producing chemical reactions. Batteries can undergo detonation, deflagration, pressure rupture, and thermal runaway--thermal explosion. The nature of the explosive reaction and the physical conditions required to initiate and propagate it depend not only upon the specific electrochemical system employed, but also upon the physical design of the battery and the battery use (discharge rate and storage).

GENERATION OF EXPLOSIVE GAS MIXTURES

Both aqueous and non-aqueous (primarily lithium) electrochemical systems can generate and accumulate potentially explosive gas mixtures. Sparking within the system initiates the explosive reaction. When initiated, these gases can undergo explosive reactions ranging from a simple burning reaction to a detonation. The severity of the explosive reaction is determined by the concentrations of the gases.

AQUEOUS ELECTROCHEMICAL SYSTEMS. In the aqueous electrochemical systems, the explosive gas mixtures produced are hydrogen-oxygen or hydrogen-air mixtures (the limits of inflammability of hydrogen in pure oxygen are between 4.65% and 93.9% by volume and in air are between 4.0% and 74.2% by volume). It is the electrolysis of the water in the electrolyte, which generates the hydrogen and oxygen gases by the following reaction:

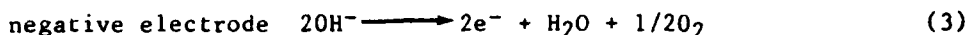


This electrolysis can occur through the phenomena of cell reversal and over-charge.

In the mercuric oxide-zinc (HgO-Zn) aqueous electrochemical system,⁸ electrolysis of water occurs during voltage reversal. Voltage reversal occurs in a series connected cell undergoing discharge, when both electrode materials

⁸DeVries, L. E., "The Cause of Explosions in Old MK 102 Mod O Batteries Under Discharge", NSWC/WOL TR 76-159, 12 April 1977.

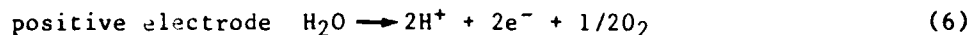
are used up. The other cells in the series circuit continue to force current through the "dead" cell. This causes the polarity of the cell to reverse. The half cell reactions are:



If gassing occurs at both electrodes, the cell reaction is reaction (1). In addition, corrosion can occur within the system, slowly generating hydrogen gas by the reaction:



In the lead dioxide-lead ($\text{PbO}_2\text{-Pb}$) system, electrolysis of water occurs during overcharge. Overcharge is the process of forcing current through a completely recharged cell. The half cell reactions are:



Again, the cell reaction is reaction (1) if gassing occurs at both electrodes.

NON-AQUEOUS OR LITHIUM ELECTROCHEMICAL SYSTEMS. In the lithium sulfur dioxide system, the explosive gas mixture produced is methane-air (the limits of inflammability of methane in pure oxygen are between 5.4% and 59.2% by volume and in air are between 5.0% and 15.00% by volume). Methane is generated by the reaction of unpassivated lithium with the solvent, acetonitrile (CH_3CN):



This reaction only occurs when the passivating film is depleted for some reason.

PRESSURE RUPTURE

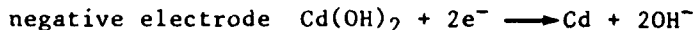
Both aqueous and lithium electrochemical systems can undergo violent pressure rupture due to either generation of gases and subsequent pressure buildup or in an increase in electrolyte vapor pressure.

GENERATION OF GASES AND SUBSEQUENT PRESSURE BUILDUP

Aqueous Electrochemical Systems. Previously, the generation of hydrogen and oxygen gases in aqueous systems was discussed for the mercury and lead acid systems. If initiation of an explosive reaction does not occur, these gases can

build up enough pressure to rupture the cell casing. An example is the nickel-cadmium (Ni-Cd) aqueous system. A discussion of this system is derived from references 9 through 14.

Due to a unique safety feature inherent to the nickel-cadmium system, the Ni-Cd cell can normally be overcharged for extended periods of time. During normal charge of cell, the following reactions occur:



During overcharge in a balanced cell, gasing occurs at both electrodes by reaction (2) and (3). The overall cell reaction is reaction (1). The result is a buildup of hydrogen and oxygen gases. The possibilities are initiation of an explosive reaction (with sparking), or pressure rupture of the cell. To make use of the safety feature of the Ni-Cd system, the cells are normally designed to be positive limited. The result is that during overcharge, some Cd(OH)_2

⁹Cahoon, N. C., and Heise, G. W., ed., The Primary Battery, Vol. 2, (New York: Wiley-Interscience Publishers, 1976), pp. 371-381.

¹⁰Lingane, J. J., Electroanalytical Chemistry (New York: Wiley-Interscience, 1958), pp. 643, 646.

¹¹Private communication with L. E. DeVries.

¹²Falk, S. U., Salkind, A. J., ed., Alkaline Storage Batteries (New York: John Wiley and Sons, Inc., 1969), pp. 277-305.

¹³Delahay, P., Tobias, C., ed., Advances in Electrochemistry and Electrochemical Engineering, Vol. 5 (New York: Wiley-Interscience Publisher, 1967), pp. 77-80.

¹⁴Evjen, J. M., "Analysis of Aircraft Battery "Thermal" Runaway," in Proceedings of the 26th Power Sources Symposium, publ 1974, pp. 99-103.

will still be present when the Ni(OH)_2 is completely electrolyzed. Therefore, gassing of oxygen only will occur (at the depleted nickel electrode by reaction (3)). The oxygen generated by reaction (3), diffuses through the cell to the cadmium electrode at which it combines with free cadmium to form Cd(OH)_2 :



By the normal half-cell charge reaction at the negative electrode (reaction (9)), Cd(OH)_2 is electrolytically reduced to free cadmium metal, which is then available to combine more oxygen as this diffuses to the negative electrode. Thus during normal overcharge there is no net chemical change occurring within the cell. Adding reactions (3) and (9) gives the following:



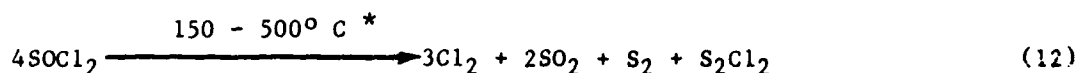
This is the cell reaction for overcharging a positive limited nickel-cadmium cell. It is also the reverse reaction of reaction (10). Adding reactions (10) and (11) gives no net reaction. Barring any malfunctions in the cyclical process, overcharge can continue indefinitely since there is continual regeneration of the Cd(OH)_2 . This prevents electrolysis of the electrolyte at the negative electrode from taking place, (reaction (2)). Therefore, if the cell has no available mechanism to recombine hydrogen gas, any failure in the cyclical overcharge can lead to pressure buildup with possible cell rupture.

One cause of failure in the overcharge is an excess of electrolyte in the cell. Too much electrolyte completely fills the passages in the separator through which the oxygen gas travels. This reduces the rate of oxygen diffusion from the positive electrode to the negative electrode. This in turn reduces the rate of oxygen combination with cadmium in reaction (10), resulting in an imbalance in the cycle of reactions and a net buildup of internal cell pressure.

Too large an excess of negative electrode material, Cd(OH)_2 , can cause a failure in the overcharge by limiting the rate of reaction (10) (consumption of oxygen). The Cd(OH)_2 tends to shield the reactive cadmium.

A leak in the seal of the cell can cause oxygen loss. This lowers the rate of Cd(OH)_2 regeneration (reaction (9)) resulting in the depletion of the negative electrode and subsequent generation of hydrogen gas.

Non-Aqueous Electrochemical Systems. As mentioned previously, the Li/SO_2 system can generate methane gas when the free lithium reacts with acetonitrile, a solvent. In the case of the lithium thionyl chloride (Li/SOCl_2) system, sulfur dioxide (SO_2) gas and chlorine (Cl_2) gas can be generated by the following reactions:



*Thermal runaway and rapid discharge can cause the cell to reach these temperatures.

INCREASE IN VAPOR PRESSURE. In both the aqueous and the lithium systems, discharge at too rapid a rate may heat the electrolyte far enough above its boiling point to produce a superheated, pressurized vapor that ruptures the battery case with considerable force.

Aqueous Electrochemical Systems. One example of an aqueous system which undergoes pressure rupture due to increase in vapor pressure, is the silver oxide-zinc system (AgO-Zn). Discharge at too rapid a rate causes this to happen. Another example is the Ni-Cd sintered battery. Under certain conditions of extended overcharge, the Ni-Cd battery and its charger can form an electrically unstable system. Some causes of this instability are high ambient temperature, and high charge voltage per cell. This instability causes increased overcharge currents. Increased current flow causes elevated cell temperatures resulting in electrolyte boiling. Vapor pressure increases until a rupture in the casing occurs. The unique feature about this system is that it will again achieve stability, following the rupture of the casing, when enough electrolyte has boiled away to significantly increase internal cell resistance.

Non-Aqueous Electrochemical Systems. The Li/SO₂ electrochemical system is an example of a non-aqueous system in which discharge at too rapid rate may result in a pressure rupture due to vapor pressure increase.

THERMAL RUNAWAY

In order to supply energy rapidly, and in the quantities demanded, batteries must be made of highly active-reactive chemicals. Metals used as anode materials are extremely reactive. A thin protective film, called a passivating film, forms on the anode surfaces due to exothermic chemical reaction of the anode material with air, electrolyte, or cathode material. The passivating film allows electrolysis to occur, but significantly reduces the rate at which the anode material reacts with other species present in the cell. Table 1 lists the chemical compositions of passivating films formed about various anodes.

TABLE 1 PASSIVATING FILMS

<u>Electrolyte Material</u>	<u>ANODE MATERIAL</u>		
	<u>Zinc</u>	<u>Magnesium</u>	<u>Lithium</u>
H ₂ O	ZnO	MgO [Mg(OH) ₂]	--
acetonitrile	--	--	Does not form a protective film
<u>Cathode Material</u>			
HgO (Alkaline)	ZnO	--	--
MnO ₂	ZnO	MgO [Mg(OH) ₂]	--
SO ₂	--	--	Li ₂ S ₂ O ₄
SOCl ₂	--	--	LiCl

Problems arise in the system when temperature elevation is sufficient to melt the anode material. Generally, the liquid state of a substance occupies a larger volume than the solid state. Therefore, as the liquid forms, its volume expands, causing the film to break apart. In addition, flowing of the liquid also breaks up the protective film. As areas of the unpassivated molten metal are exposed to the electrolyte, energetic chemical reactions take place, generating heat. The flowing, expanding liquid metal, creates a greater surface area on which exothermic chemical reactions can take place. The overall effect is that heat is generated, increasing the kinetics of the energetic reactions occurring. As more and more heat evolves, the rate of energetic chemical reactions continues to increase. There is then the possibility of a thermal runaway and or thermal explosion. Even if thermal explosion does not occur, there is danger of fire and/or violent pressure rupture due to evolution and/or increase of gas pressure.

In the aqueous electrochemical systems, there is little danger of melting the anode material, except in incineration. The reason is because these anode materials have such high melting points ($T_m = 419.5^\circ\text{C}$ for zinc, and $T_m = 651^\circ\text{C}$ for magnesium). In non-aqueous systems, the anode material is lithium, which has a much lower melting point (180.6°C).

NON-AQUEOUS ELECTROCHEMICAL SYSTEMS. The lithium anode electrochemical systems have the highest energy densities of any electrochemical systems presently in use. The following discussion is derived from references 15 - 26.

¹⁵Bowers, F. M., "Safe, Useful Lithium Batteries for the Navy," NSWC/WOL TR 77-140, 15 December 1977.

¹⁶Schlaikjer, C. R., et. al., "Discharge Reaction Mechanism in the Li/SOCl₂ Cells," Electrochemical Society, Journal of the, 126, 513, (1979), p. 513.

¹⁷Taylor, H., and Bowden, W., "Li/SO₂ Cells Improved Stability," in Proceedings of the 28th Power Sources Symposium, publ 1978, pp. 184-187.

¹⁸Kilroy, W. P., "The Chemistry of the Li-SO₂ Battery-A Review," in Proceedings of the 28th Power Sources Symposium, publ 1978, pp. 198-202.

¹⁹Dey, A. N., "Lithium Anode Film and Organic and Inorganic Electrolyte Batteries," Thin Solid Film, Vol 43, 1977, p. 131.

²⁰Chua, D. L., and Merz, W. C., "Lithium Passivation in the Thionyl Chloride System," in Proceedings of the 27th Power Sources Symposium, publ 1976, pp. 33-36.

²¹Dey, A. N., "Primary Li/SOCl₂ Cells VI. Identification of the Possible Explosion Causing Cell Constituents by DTA Studies," in Proceedings of the 28th Power Sources Symposium, publ 1978, pp. 251-255.

²²Damlit, M., and Ablard, J. E., "Chemistry of Detonations. II. Buffered Equilibria," The Journal of Chemical Physics, Vol. 48, No. 1, pp. 41-42.

²³Private communication with Stanley James.

²⁴Besenhard, J. O., and Fritz, H. P., "Cathodic Reduction of Graphite in Organic Solutions of Alkali and NR₄⁺ Salts," Electroanalytical Chemistry and Interfacial Electrochemistry, 53, (1974), 329-333.

²⁵Mills, K. C., Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides, 1974, p.

²⁶Nebergall, W. H., Schmidt, F. C, Holtzclaw, Jr., H. F., General Chemistry, pp. 930-931.

During normal discharge in the Li/SOCl₂ system, the following net reaction is thought to occur:



The electrolyte is thionyl chloride with dissolved lithium tetrachloroaluminate (LiAlCl₄).

During normal discharge, the following reaction occurs in the Li-SO₂ electrochemical system:



The electrolyte contains either propylene carbonate (PC) and acetonitrile (AN), or AN alone as solvents, with SO₂ as the active cathode material. The electrolyte is either lithium bromide (LiBr) or lithium hexafluoroarsenate (LiAsF₆).

In the Li/SOCl₂ system, the passivating film which forms on the lithium anode is lithium chloride (LiCl). In the Li-SO₂ system, this film is thought to be lithium dithionite, Li₂S₂O₄. Any continuous breakdown of the anode passivating film can allow lithium to react energetically and exothermically with species present in the cell and ultimately initiate thermal runaway. The major cause of such a breakdown is heat generation sufficient to melt the anode. There are basically two major sources of heat generation sufficient to melt the anode. The first is voltage reversal, and the second is discharge at too rapid a rate, especially short-circuit.

In addition, temperatures capable of melting sulfur, but not lithium, have in some cases resulted in thermal runaway. It is believed that this is because molten sulfur chemically or physically breaks down the passivating film.

Voltage Reversal. Cell reversal can lead to the generation of certain species which in turn can initiate thermal runaway. Under cell reversal, species within the cell, other than the anode and cathode material, must be oxidized and reduced. For example, the lithium ion (Li) in the electrolyte can plate out on the carbon substrate by the following reaction:



It is uncertain whether the plated lithium actually forms a compound with the carbon, or whether it is finely divided among the carbon substrate. Either way, the "LiC" association acts as a highly reactive intermediate in many exothermic chemical reactions which can occur at the carbon substrate.

Short Circuit. Sufficient heat to initiate a thermal runaway occurs when a battery is discharged at too rapid a rate for the design. An internal short may allow contact between anode and current collector. The result is a high current flow. This can result in hot spots which can melt the lithium anode.

In an external short-circuit, there may or may not be localized current flow and, therefore, hot spots may or may not be generated. However, the heat generated by I^2R heating is still sufficient to initiate thermal runaway.

EXOTHERMIC CHEMICAL COMBINATIONS. The heats of reaction (ΔH) of several exothermic chemical reactions in the Li/SO_2 and Li/SOCl_2 batteries are compared in Table 2 to the heat of detonation of TNT. It is interesting to note that the lithium reactions release ten times more heat than the detonation of TNT. However, one must keep in mind that these reactions occur at much slower rates than the detonation of TNT.

TABLE 2: THERMODYNAMIC DATA OF SEVERAL EXOTHERMIC COMBINATIONS WHICH CAN OCCUR IN THE Li/SO_2 AND Li/SOCl_2 ELECTROCHEMICAL SYSTEMS

EXOTHERMIC CHEMICAL REACTION	ΔH OF REACTION (Kcal/gLi)	ΔH OF DETONATION OF TNT (Kcal/g)
$2\text{Li} + \text{S} \longrightarrow \text{Li}_2\text{S}$	-7.68	-.9 to -1.0
$2\text{Li} + 2\text{H}_2\text{O} \longrightarrow 2\text{LiOH} + \text{H}_2$	-13.9	
$6\text{Li} + \text{SO}_2 \longrightarrow \text{Li}_2\text{S} + 2\text{Li}_2\text{O}$	-7.45	
$2\text{Li} + 2\text{SO}_2 \longrightarrow \text{Li}_2\text{SO}_4 + \text{S}$	-13.7	
$2\text{Li} + \text{Br}_2 \longrightarrow 2\text{LiBr}$	-12.1	

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