ENERGY CONVERSION BY SPONTANEOUSLY REACTING Li–SO$_2$ CELLS

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Summary

In abuse tests Li–SO$_2$ cells were exploded in a detonation chamber and in calorimeters. The energy measurements show that when air is present, the energy released is six times that obtained by electrically discharging the cells. In the absence of air the energy is reduced to one third.

Reactions which may perhaps occur in the two cases are described and the heats of reaction are calculated. The calculated values are in fair agreement with those obtained experimentally.

By comparing the pressure increase, it has been shown that the cell explosion is not as fast as the detonation of TNT. It is, however, faster than the combustion of the gunpowder used for comparison.

1. Introduction

Batteries based on the Li–SO$_2$ system have electrical properties which are far superior to most other batteries [1 - 4]. The energy density is as high as 300 W h/kg [4], it is capable of operating at power levels of 460 W/kg while delivering 100 W h/kg [5], and the low temperature performance is good. At −40 °C it is still able to deliver about 50% of its room temperature capacity [4].

Sometimes, however, unexpected reactions may occur which result in failure of the system, fire, or even explosions [6]. Even though the projected shelf life is 5 - 10 years [4], cells are sometimes found not to function within one year of the production date [7]. Usually this is due to ventilation, *i.e.*, release of SO$_2$. In many cases this is caused by external corrosion, especially in the vicinity of the vent. On occasions, however, the SO$_2$ release is caused by an increase in pressure within the cell. Subsequently it is usually difficult to trace the origin of the reaction which has caused the pressure increase.

Even though slow ventilation is undesirable, it will not normally harm individuals. On one unfortunate occasion in 1976, however, some Norwegian

soldiers were injured [6, 8]. The release of SO_2 caused strong local irritation of the upper respiratory trachea. The injury was not, however, characterized as serious [8]. Sulphur dioxide is highly corrosive and may cause damage to equipment. It is also poisonous, but fortunately it can easily be detected by smell and taste at levels as low as 1 ppm [9].

The situation becomes much more serious when fire occurs. This may, for instance, occur when the cells are overdischarged [10, 11]. In order to simulate the situation which occurs when a cell within a battery pack has been driven in reverse by the other cells, a cell was thermally insulated and then force discharged. After complete discharge, the cell was further force discharged by a high current. By this treatment, the temperature of the cell was observed to increase sharply and the cell vented explosively.

As pointed out by Di Masi [10], the useful life of the cell is either limited by the carbon surface area at the cathode, by the amount of SO_2 or of Li. Sulphur dioxide was the limiting factor in the explosively vented cells. Di Masi explains the explosive ventilation by assuming that a reaction between Li and the acetonitrile in the electrolyte takes place when SO_2 is absent. Methane is then formed. Dey *et al.* [12 - 14] have shown by differential thermal analysis that this reaction is exothermic at room temperature. The reaction is, however, hampered by the presence of SO_2. Since the conductivity of the electrolyte in the cell is greater the higher the concentration of SO_2, the temperature in the cell without SO_2 will increase sharply when a current is forced through it. The instability of the system, together with the increase in temperature, was thought to be the reason for the explosion. Di Masi [10] was able to show that when the cell capacity was limited by Li instead of by SO_2, the explosive ventilation could be avoided. He called such cells "balanced cells" and such cells are now in common use.

An even more violent explosion is described by Taylor *et al.* [5]. It occurs when the cell is discharged, then charged and further overcharged. A cell, not previously discharged, will not explode or vent by overcharging. The explosion was explained by assuming that when a discharged cell is charged, finely divided and freshly plated Li will be formed on the anode. Bromide ions from the dissolved LiBr will be oxidized to Br_2 on the cathode. This Br_2 is soluble in the electrolyte and may diffuse to the anode where it will react with the freshly formed Li. This will result in an explosion.

From an energy point of view, an overcharged cell should be in its most dangerous state. Lithium will then be metallic and therefore very reactive. Sulphur dioxide, which is present in the charged state, is also more energy dense than $S_2O_4^{2-}$ which is present in the discharged state. If an explosion occurs in the charged state therefore, it will probably be more violent than explosions occurring in any other states of the Li–SO_2 system. From a safety point of view, it is important to know the energy release and speed of the explosion. It is also important to determine whether precautions can be taken to reduce the action of the explosion.

With this in mind, experiments have been conducted in which the cells were handled as explosives and the energy released during the explosion was

measured. In order to obtain a reproducible explosion, the cells were handled in a way that hopefully will not take place in normal practical use.

2. Experimental

Commercial Li–SO$_2$ single cells from two different manufacturers were used in the experiments. The cells were of different sizes and ranged in nominal capacity from 1 to 24 A h. Only cells of nominal capacities 2.3 and 24 A h are reported on here, however. The cells were not insulated.

All the cells were discharged with a constant current controlled by an external power supply. Several different currents were used, but the discharge time was kept nearly constant at 20 h. The cells were then charged at constant current. When the cells had been charged to 120% of their nominal capacity, the charging current was increased to approximately 0.5 C. Within 10 min the cells would normally explode.

In order to measure the energy released, the cells were placed in either a detonation chamber, a closed vessel bomb, or a calorimetric bomb.

The detonation chamber was a 1 m^3 hermetically sealed cylindrical steel drum. It was equipped with a pressure transducer in order to measure the pressure inside the chamber. A thermocouple was placed in the top section of the chamber in order to measure its wall temperature.

The closed vessel bomb had a volume of 150 cm^3. Only the pressure inside the bomb was measured *vs.* time. In order to obtain fast measurements, a transient recorder, Biomation mod 1015, equipped with pretriggering facilities, was used. This allows the pressure increase itself to be used as a trigger signal.

The calorimeter bomb had a volume of 450 cm^3. It was placed in a vessel filled with polystyrene foam for thermal insulation. The temperature of the calorimeter was recorded as a function of time by an ordinary strip chart recorder.

The detonation chamber was calibrated by exploding different charges of TNT. The calorimeter was calibrated by burning benzoic acid in O$_2$. The O$_2$ pressure was 25 atm.

The closed vessel bomb was in reality not calibrated. The results from the exploding cells were merely compared with corresponding results from different charges of gunpowder.

3. Results

Figure 1 shows the post-detonation pressure in the detonation chamber for different loadings of TNT. As can be seen, a maximum pressure is reached quite rapidly. After passing through the maximum, the pressure decreases slowly. The decreasing portions of the curves are seen to be parallel for the different loadings. This indicates that the pressure at any time after the
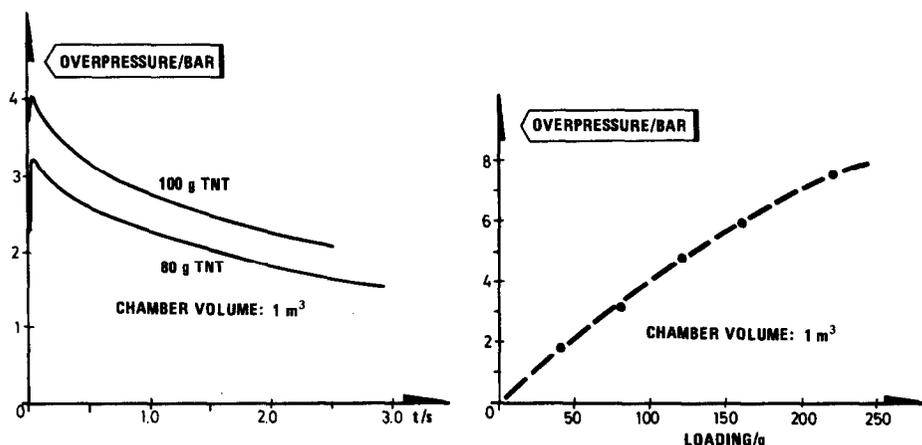
Fig. 1. The post-detonation pressure in the detonation chamber as a function of time. Two different loadings of TNT are shown.

Fig. 2. The maximum post-detonation pressure in the detonation chamber as a function of the TNT loading.

maximum can be related to the size of the loading. Since the volume of the air inside the chamber is much larger than that required to give complete combustion, the pressure can also be related to the energy of the reaction.

In Fig. 2 the maximum pressure obtained during a detonation is plotted *vs.* the amount of TNT. As can be seen, the curve deviates somewhat from a straight line.

In Fig. 3, the TNT has been replaced by a 24 A h Li–SO$_2$ cell. When the curve is compared with those in Fig. 1, it can be seen that the pressure increase is much slower for the cell than for TNT. This indicates that the cell explosion is much slower than the explosion of TNT. After a while, the pressure curve becomes almost identical with that of 100 g of TNT. This indicates that the energy released by the exploding 24 A h cell corresponds to that of 100 g of TNT.

The temperature change of the chamber wall is plotted *vs.* the time after an explosion in Fig. 4. As can be seen, a fairly stable maximum temperature is obtained. The temperature decrease after the maximum is very slow.

The stable maximum temperature change of the wall *vs.* the amount of TNT is shown in Fig. 5. The straight line obtained, indicates a simpler relationship than that obtained with the pressure. The result obtained with an exploding 24 A h Li–SO$_2$ cell is shown in the same Figure. These experiments also show that the energy released when the cell explodes corresponds to that of 100 g of TNT.

Since the volume of the detonation chamber is large, an excess of O$_2$ is present. In order to check whether O$_2$ is important for the cell explosion or not, cells were exploded in the small, closed vessel bomb. In this bomb the air volume is too small to play any role. In these experiments 2 A h cells were used.
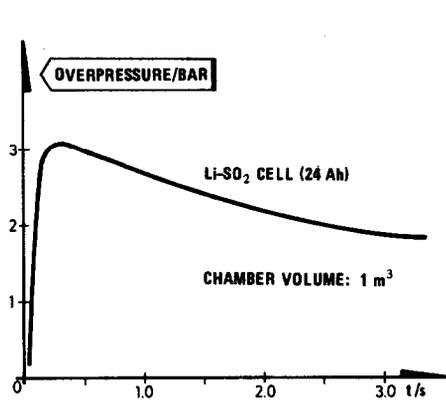
OVERPRESSURE/BAR

Li-SO$_2$ CELL (24 Ah)

CHAMBER VOLUME: 1 m^3

ΔT/(°C)

t/s

t/min

Fig. 3. The post-detonation pressure caused by an explosion of a 24 A h Li–SO$_2$ cell in the detonation chamber.
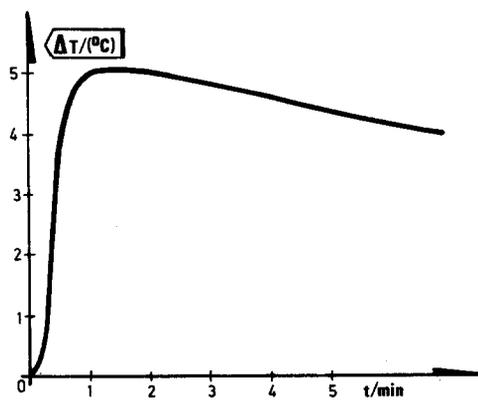
Fig. 4. The temperature change of the detonation chamber wall *vs.* time after explosion. 100 g of TNT.

ΔT/°C

THE INCREASE BY THE 24Ah CELL

CHAMBER VOLUME: 1 m^3

LOADING OF TNT/g

PRESSURE/BAR

6 g GUN-POWDER

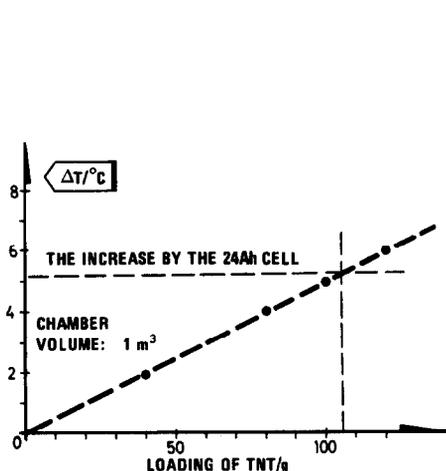2 Ah Li-SO$_2$ CELLS

4 g GUN-POWDER

t/ms

Fig. 5. The temperature increase of the detonation chamber wall for different TNT loadings. The value of the 24 A h Li–SO$_2$ cell is incorporated.
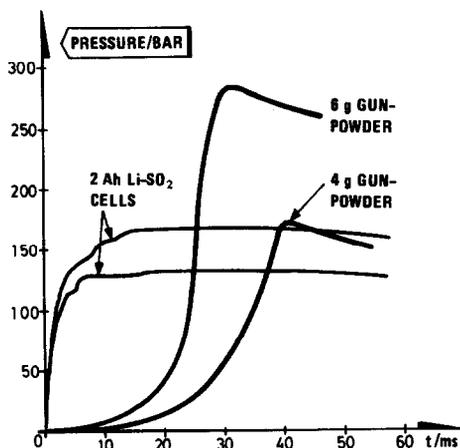
Fig. 6. The post-detonation pressure in the closed vessel bomb as a function of time.

The pressure *vs.* time curves for two cell explosions are shown in Fig. 6 together with the pressure curves obtained with two different loadings of gunpowder (type M-10). If the results from the detonation chamber, *i.e.*, with excess oxygen, are used as the basis for the calculations, the cells should contain much more energy than the gunpowder, which does not need oxygen. As Fig. 6 shows, however, the pressure obtained with the cell explosion indicates that less energy is released than with gunpowder. The energy released by the cells seems therefore to be strongly reduced when the cells are exploded in the absence of air. However, an exact figure for the released energy

cannot be obtained from these experiments. This is due to the fact that the composition of the air inside the closed vessel bomb will be considerably altered by the reactions. The pressure increase will therefore not give a reliable means of determining the energy release. The results therefore merely give indications of the energy release rather than exact data.

In addition to an indication of the energy release, the Figure also gives an indication of the reaction rates. As can be seen, the pressure increase for the cell explosions is much faster than for the gunpowder reaction. This indicates that the cells react more quickly.

In order to obtain more quantitative information about the energy release when insufficient air is present, the calorimetric bomb was used. The heat capacity of the bomb was determined by burning benzoic acid in O_2. Figure 7 shows the temperature change of the calorimeter as a function of time after the combustion of 1.524 g of benzoic acid.

A similar curve is shown, for an exploding lithium cell in the same Figure. The temperature increase is shown to be 1.2 °C higher than that obtained with the benzoic acid. The energy released is therefore somewhat higher when the cell explodes.
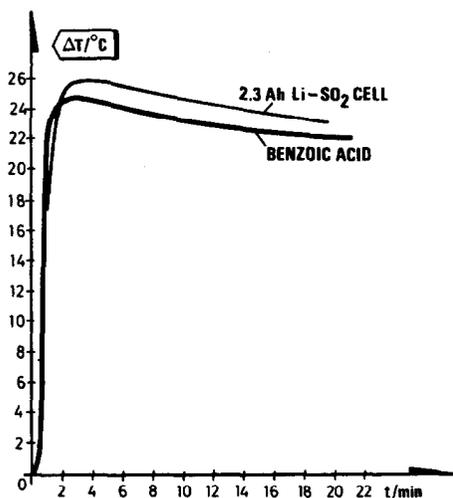

Fig. 7. The temperature increase in the bomb calorimeter caused by combustion of 1.524 g of benzoic acid in O_2 at 25 atm pressure and an exploding 2.3 A h Li–SO$_2$ cell.
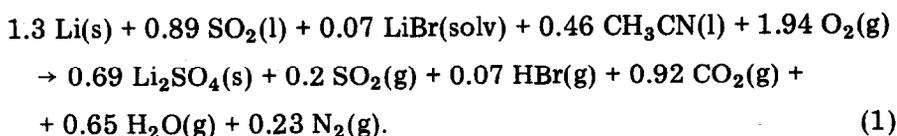
4. Discussion

The experiments in the detonation chamber show that if excess air is present, the energy released by the 24 A h Li–SO$_2$ cell corresponds to approximately 100 g of TNT. The explosion of TNT in the detonation chamber has previously been treated by Strømsøe [16]. From experimental data he has calculated the heat of explosion in Ar (860 cal/g), in N$_2$

(940 cal/g) and in air (3220 cal/g). The last figure is close to the theoretical heat of combustion for TNT (3480 cal/g). If the calculated value for the heat of explosion in air is used for TNT in our experiments, the heat produced by the explosion of the 24 A h cell should be approximately 320 kcal since the cell explosion corresponds to approximately 100 g of TNT.

The 24 A h cell will be approximately 2.4 times larger than the 10 A h D-cell. The D-cell contains approximately 3.8 g of Li, 24 g of SO_2, 2.4 g of LiBr and 7.8 g of CH_3CN (acetonitrile). The corresponding values for the 24 A h cell should therefore be approximately 9 g of Li, 57 g of SO_2, 6 g of LiBr and 19 g of CH_3CN. This corresponds to 1.3 mol of Li, 0.89 mol of SO_2, 0.07 mol of LiBr and 0.46 mol of CH_3CN.

When excess air is present and it is assumed that most of the compounds take part in the combustion, the following total reaction might perhaps take place:

$$1.3 \text{ Li(s)} + 0.89 \text{ SO}_2\text{(l)} + 0.07 \text{ LiBr(solv)} + 0.46 \text{ CH}_3\text{CN(l)} + 1.94 \text{ O}_2\text{(g)}$$

$$\rightarrow 0.69 \text{ Li}_2\text{SO}_4\text{(s)} + 0.2 \text{ SO}_2\text{(g)} + 0.07 \text{ HBr(g)} + 0.92 \text{ CO}_2\text{(g)} +$$

$$+ 0.65 \text{ H}_2\text{O(g)} + 0.23 \text{ N}_2\text{(g)}. \tag{1}$$

From this the heat of reaction can be calculated if the heat of formation of the constituents is known, *i.e.*,:

$$\Delta H = 0.69 \ \Delta H_f^\circ(\text{Li}_2\text{SO}_4) + 0.2 \ \Delta H_f^\circ(\text{SO}_2) + 0.07 \ \Delta H_f^\circ(\text{HBr}) +$$

$$+ 0.92 \ \Delta H_f^\circ(\text{CO}_2) + 0.65 \ \Delta H_f^\circ(\text{H}_2\text{O}) + 0.23 \ \Delta H_f^\circ(\text{N}_2) -$$

$$- 1.3 \ \Delta H_f^\circ(\text{Li}) - 0.89 \ \Delta H_f^\circ(\text{SO}_2) - 0.07 \ \Delta H_f^\circ(\text{LiBr}) -$$

$$- 0.46 \ \Delta H_f^\circ(\text{CH}_3\text{CN}) - 1.94 \ \Delta H_f^\circ(\text{O}_2). \tag{2}$$

If the appropriate values for the heats of formation [17, 18] are introduced into eqn. (2), the heat of reaction is found to be —307 kcal. Comparison of this result with the heat observed in the detonation chamber (320 kcal) provides fair agreement.

Some deviation from the experimental results is to be expected since the latter are performed at constant volume and not at constant pressure. The effect of this would be to give calculated values somewhat below those observed. In addition, $\Delta H_f^\circ(\text{LiBr(solv)})$ used in the calculation is the standard value of LiBr dissolved in H_2O and not in the electrolyte. Since the errors are, however, small, compared with the experimental errors, no corrections are found to be necessary.
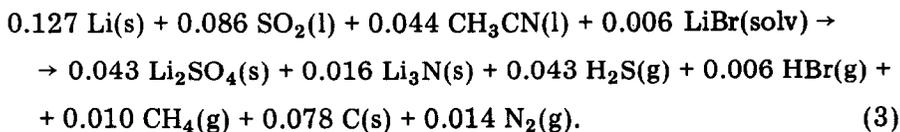
The electric energy delivered by the cell will be 67 W h, provided that the mean cell voltage is 2.8. This corresponds to 58 kcal, which is only between 1/5 and 1/6 of the energy released by the explosion.

Since the energy measured corresponds well with that expected from eqn. (1), this reaction is probably valid for the cell explosion. As reaction (1) shows, the oxygen content of the surrounding air seems to play an important

part in the cell explosion. Since this is not involved in the cell discharge process, a lower energy is therefore to be expected.

The energy released during the cell explosion in the absence of significant air was tested in the 450 cm^3 calorimetric bomb. The benzoic acid used for calibration was standardized for calorific purposes and had a heat of combustion equal to 6318 cal/g. From Fig. 7 it can be seen that the temperature increase was 24.7 °C when 1.524 g of benzoic acid was combusted. This gives a bomb heat capacity equal to 389.8 cal/deg.

When the 2.3 A h $Li-SO_2$ cell was exploded in the bomb, the temperature increase was 26 °C, which indicates that the energy released during the explosion was approximately 10 kcal. Assuming a cell voltage equal to 2.8, the electric energy which the cell can deliver will be 5.5 kcal, which means that only double the amount of energy is released during the explosion. Since the electrical energy content in the 2.3 A h cell is somewhat less than 1/10 of that exploded in the detonation chamber, the energy released during the explosion of the 2.3 A h cell in the presence of sufficient O_2 should be approximately 30 kcal. The absence of O_2 has obviously reduced the energy release to approximately 1/3 of that if O_2 had been present. The reaction which will perhaps take place in the absence of O_2 is given by eqn. (3), *i.e.*,:

$$0.127 \text{ Li(s)} + 0.086 \text{ SO}_2(\text{l}) + 0.044 \text{ CH}_3\text{CN(l)} + 0.006 \text{ LiBr(solv)} \rightarrow$$

$$\rightarrow 0.043 \text{ Li}_2\text{SO}_4(\text{s}) + 0.016 \text{ Li}_3\text{N(s)} + 0.043 \text{ H}_2\text{S(g)} + 0.006 \text{ HBr(g)} +$$

$$+ 0.010 \text{ CH}_4(\text{g}) + 0.078 \text{ C(s)} + 0.014 \text{ N}_2(\text{g}). \tag{3}$$

The heat of reaction can now be calculated on the basis of the heats of formation [17, 18]. The expected heat of reaction for eqn. (3) is then found to be −9.33 kcal, which corresponds fairly well with the observed 10 kcal.

In the experiments described above, the cells were exploded by charging them following a discharge. The experiments have shown that the effect of the explosion can be reduced to one third by excluding air.

Even though other reactions probably take place when other procedures are used to promote explosion, for instance, by overdischarging the cells, it is very likely that combustion in air also plays an important role in these cases. If, therefore, explosions are likely to occur, either in tests or in actual use, damage can probably be reduced if air can be excluded from the cell surroundings, for instance, by the presence of inert gas.

5. Conclusion

When $Li-SO_2$ cells are exploded by charging, the energy released is approximately 6 times that delivered by the cells during electrical discharge. Most of the energy is due to combustion in air. When air is excluded, the energy release can be reduced to 1/3 of that obtained in the presence of air. If the air surrounding the cell is replaced by an inert gas therefore, the effect of an explosion will probably be reduced.

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