

Exposure of lithium batteries to external hydrostatic pressure

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Abstract: A battery containing 294 cells in the form of 7 modules of 42 DD lithium / sulfuryl chloride cells in a 7S6P configuration exploded during pigging of a 30" gas pipeline in April 1999. The gas pressure in the pipeline was ca 160 Bar. It is likely that the explosion was caused by a leak in the battery container. This paper describes the behavior of the 30 Ah lithium / sulfuryl chloride DD cell (CSC93) under hydrostatic compression (in water and in inert gas), the effect of state charge and the effect of potting

Keywords: Lithium sulfuryl chloride cells; battery safety; battery design; pipeline inspection

Introduction

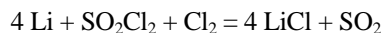
Lithium battery powered pipeline inspection tools ("Pigs") are used by the oil and gas industry for internal inspection of pipelines. Usually, the battery is confined within a sealed unit. If this seal develops a defect, an internal rise of pressure takes place until the external pressure is approached. A battery containing 294 cells in the form of 7 modules of 42 DD lithium / sulfuryl chloride cells in a 7S6P configuration exploded during pigging of a 30" gas pipeline in April 1999. The gas pressure in the pipeline was ca 16 MPa (160 Bar). Larger batteries, based on 567 cells, are in use in 40" pigs. Similar batteries are used as emergency power in diver habitats.

Increasing the external pressure has the following consequences on a lithium cell:

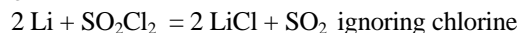
- The opening temperature of the safety valve increases
- Collapse of the cell-can may result in an internal short
- In the presence of water, water ingress makes the cell unstable

Main concerns by the users of these batteries are gas leaking into battery containers and exposure of the battery containers to fire during transport and storage

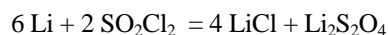
The cell chemistry is [1,2]:



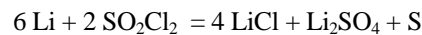
or



A cell reaction producing elemental sulfur has also been suggested by Razzini et al. [1]. They detected elemental sulfur after discharge of a sulfuryl chloride cell (no chlorine in the electrolyte).



The dithionite decomposes into sulfate and sulfur giving



Experimental

The CSC 93 cell and the 3PD0524 module are produced by Wilson Greatbatch / Electrochem Industries. The cell is 111 mm long and 33.6 mm in diameter. The cell is protected by an internal fuse and shunt diode in the lid and a safety valve. Cell weight is ca 214 g. Each module contains 21 cells as 3 parallel strings of 7 serially connected cells (7S3P configuration). The module has a serial diode and a fuse in each string and a temperature breaker (104°C) in the negative lead. The cells in the module are potted in an elastomer. Module weight was 6.141 kg. In order to charge one string, the potting was partly removed and the temperature breaker and serial diode were bypassed.

The cells were compressed in a container with 50 mm internal diameter and a volume of 360 ml and a safe pressure rating of 120 MPa. Figure 3 shows the tank after a cell explosion. The pressure container was either connected to a Shimadzu High Pressure Liquid Chromatography (HPLC) pump using deionized water or a bottle of compressed nitrogen (15 to 20MPa). Stainless steel tubing of 0.3 mm internal diameter was used between the pump or the gas bottle and the pressure vessel. The HPLC pump switched off automatically at 40 MPa. Weak bolts were used so that a pressure in excess of 60MPa stretched the bolts, allowing the O-ring in the lid to open as a safety valve. Some cells were potted in silicone rubber (Elastosil RT607 (Wacker)) ahead of pressurization.

Pressure, temperature and cell voltage were logged at 5 Hz, in later experiments also at 96 kHz during rapid change of values. In some experiments, the cells were discharged during test with 3ohm. At least 3 parallel experiments were made.

Cells at 50 % SOC (State of Charge) were produced from fresh cells discharged for 15 Hr at 1.00A ahead of the experiments. Cells at 0 % SOC were discharged to 2.50 V at 1.00 A.

Results

Figure 1 shows the pressure versus time graph for a cell at 0% SOC. The flow rate of water is 2 ml/minute, gradually expanding the container and compressing the cell until something breaks at a pressure of ca 8 MPa. Initially the

pressure rises non-linearly as the cell is compressed, then something breaks and the pressure increase stops. Subsequently the cell exploded. Note the difference in slope of the curve during the initial and the final phase of the compression. In the final phase only solid and liquid materials are present. At 40 MPa the pump is stopped. Figure 2 shows the delay between the collapse and the explosion. Initially the cell voltage falls gradually from 2.95V to 2.0V, and then the cell explodes.

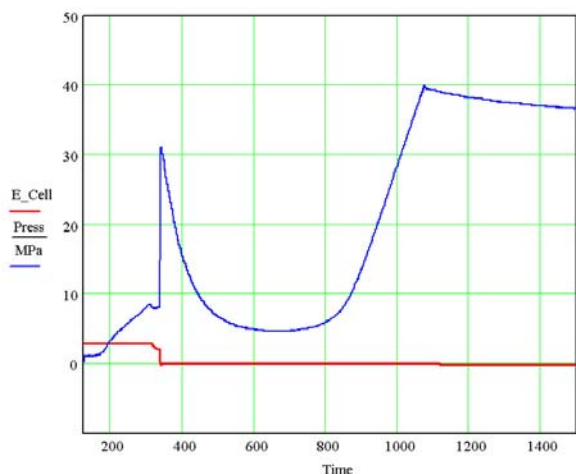


Figure 1. Discharged cell pressurized with water at a flow of 2 ml/min. Cell voltage/V and pressure/MPa versus time/s

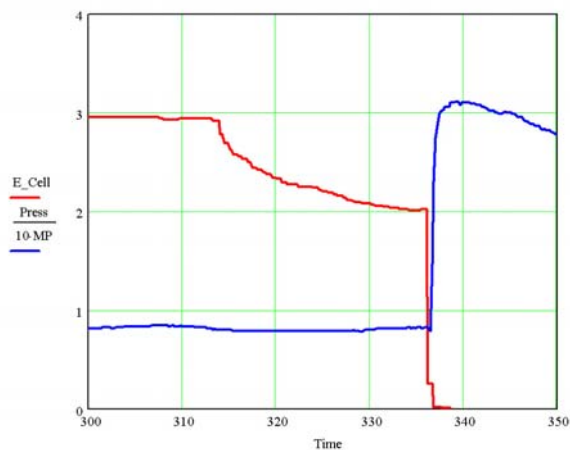


Figure 2. Enlarged part of cell voltage / V and pressure / 10 Pa versus time / seconds. Same experiment as in Figure 1.

Figure 3 shows the pressure vessel after pressurizing a cell at 50% SOC. In this case, the pressure increased above

60 MPa and the hot gases burned their way through the aluminum lid and body, creating a ca 2 cm² hole and completely destroying the pressure vessel.

Pressurization of fresh cells did not lead to explosions and the heat evolution was insignificant. After the test, the cells leaked electrolyte from the top (positive terminal) and showed a concave cell bottom. Figure 4 shows the pressure versus time curve for a fresh cell.



Figure 3. Pressure vessel after pressurizing a cell at 50% SOC with water at a flow of 2 ml/min.

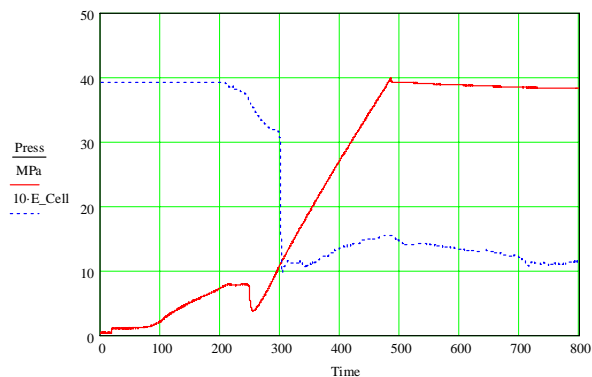


Figure 4. Pressure/MPa and open circuit cell voltage versus time/s. Fresh cell. Water flow 2 ml/min.

Discharged cells and cells at 50% SOC exploded, fresh cells did not. Collapse pressure was 7.28 MPa with a standard deviation of 0.24 MPa (n=8).

Subsequently cells at 0, 50 and 100 % SOC were pressurized with nitrogen gas. None of these cells exploded, but leaked electrolyte after the test. Collapse

pressure in these experiments was difficult to determine and the cell voltage was also unaffected.

Battery modules used in pigs are completely encapsulated in a rubber-like material. In the next experiment the cell was encapsulated in ca 5 mm thick silicone rubber. Figure 5 shows the pressure and cell voltage during the test and figure 6 the cell after the test.

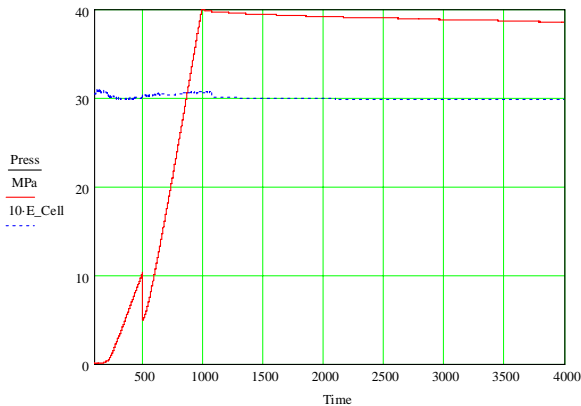


Figure 5. Pressure/MPa and cell voltage versus time/s. 100% SOC, load 3 ohm. Water flow 2 ml/min.



Figure 6. Cell after the experiment in fig 5. Left with potting, right after the removal of the potting.

Potting of the cell resulted in an increase in the collapse pressure from 7.28 MPa to 10.29 MPa with a standard deviation of 0.7 MPa (n=9). The damage to the cell was also changed. In addition to the indentation in the bottom of the cell, the cylinder wall collapsed. Of the three potted cells at 50% SOC, one exploded immediately at the

collapse pressure, one exploded after 14.7 hours and one cell did not explode. Of three fresh cells and three completely discharged cells, none exploded.

Figure 7 shows the pressure and cell voltage versus time for one potted cell at 50% SOC pressurized in nitrogen.

From the high speed recording, the collapse pressure was 10.0 MPa and the peak pressure 59.7 MPa. The time between collapse and pressure increase was 46 msec.

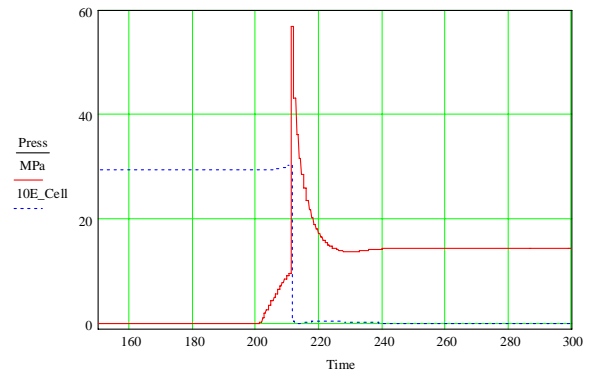


Figure 7. Pressure/MPa and cell voltage versus time/s. 50 % SOC, load 3 ohm. Nitrogen gas.

Nail penetration: Three discharged cells, three at 50% SOC and three fresh cells all exploded when tested. Cells at 50% SOC exploded most violently.

Heating: Heating fresh cells at 4°C/min resulted in a mild venting (no flame). At 50% SOC a violent venting with flames was observed.

A battery container with one fresh **7S3P** module was heated with a propane torch. Figure 8 shows the resulting temperature and pressure in the container as well as the module voltage versus time.

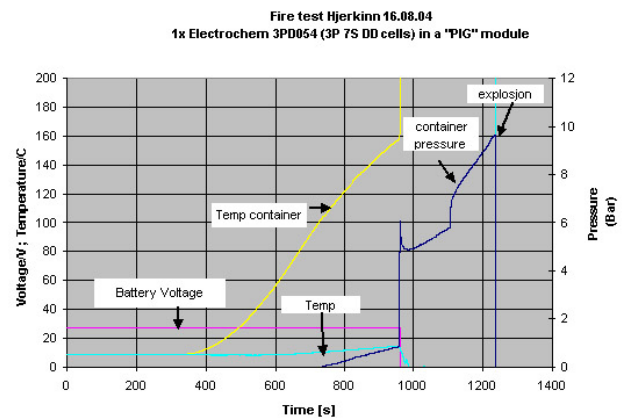


Figure 8. 21 cell battery module in battery container. The container is heated externally by a propane torch.

It is evident from the figure that at least two ventilations occurred (destroying the temperature sensor), then the container exploded. Rupture pressure was calculated to ca 7 MPa. Post analysis showed that only 4 cells exploded, 5 cells had vented (developed a leak) and 12 cells were OK, but with compression damage in the bottom of the cell.

In strong contrast to the findings by Liang et al [2], charging was found to be a reproducible way of bringing the cells to explosion. Typically the cell exploded after 2 hours at 2 A and room temperature. If the external temperature was lower, the time to explosion was longer. Charging heated the cell to ca 90°C measured at the side of the cell at the time of explosion.

In a different experiment, one string of 7 cells in one module was charged with 2 A in a battery container with 3 modules (63 cells). The battery container exploded after 2.5 hours. After the experiment, 6 cells had exploded, 30 cells had vented (leaked) 26 were OK, but with compression damage in the bottom. One cell was not found.

Discussion

One immediate result is that bare cells exposed to external pressure develop a leak in the top of the cell. This leak is via the glass to metal seal or the safety valve and allows gas or liquid to enter the cell. This removes mechanical forces on the cell. With water, partly and fully discharged cells explode some time after the collapse. With nitrogen nothing happens after the leak has developed. Why water penetration into fresh cells did not result in a significant rate of heat production is not understood. Even the reaction of sulfuric acid with water is exothermic [4], resulting in a production of sulfuric and hydrochloric acid.

When the cell is potted, potting seals off the top and the cylinder wall collapses. This takes place at a significantly higher pressure (but still below the operating pressure of a gas pipeline). Whether this results in an internal short or not may be completely accidental. If internally shorted, the cell explodes immediately as shown in figure 7.

There is an indication that partly and fully discharged cells are more dangerous than fresh cells if compressed hydrostatically. This is also the case when the cells are exposed to external heating. Fresh cells vented in a benign way at ca 120°C, cells at 50% SOC vented violently with flames. A fresh cell that vents, distills off the oxidant completely. Assuming that sulfur or $\text{Li}_2\text{S}_2\text{O}_4$ have been formed during discharge [1], this stays in the cell and can react violently with lithium.

Thus the common practice of discharging modules sequentially has a safety advantage as well as an economic advantage as only discharged modules are scrapped.

In a sealed battery container exposed to fire, the pressure build-up from the initial cell venting increases the venting temperature for the next cell etc until finally an explosion takes place. This is irrespective of the state of charge of the battery. The positive finding is that usually there are sufficiently large temperature gradients in the battery container so that only a small number of cells explode.

Thus a safety assessment based on the total battery energy is probably unnecessarily conservative.

Conclusion

For some applications, there are no good alternatives to the lithium sulfuric acid system. However, a few steps can be taken to increase system safety:

Potting of cell tops should not be done in batteries that may accidentally be exposed to external pressure.

Sequential discharge of battery modules may save money and increases safety.

It is good practice to use a weak lid or safety valves on battery containers [3]. During transport and storage, high pressure battery containers should not have their lids bolted.

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