

PERFORMANCE VERSUS SAFETY OF SOME PRIMARY AND RECHARGEABLE LITHIUM BATTERIES

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ABSTRACT

The performance and safety of selected portable, military batteries is discussed, with emphasis on extreme physical and electrical abuse tests, such as nail penetration and overcharging. The battery couples discussed are the lithium-sulphur dioxide and lithium-manganese dioxide non-rechargeable systems plus the nickel-metal hydride and lithium-ion rechargeable systems.

1. INTRODUCTION

Military forces are faced with a variety of battery chemistries for replacing older battery types, or when choosing one for new, power hungry equipment. Although rechargeable batteries are preferable, at the present time only primary (non-rechargeable) batteries will meet the requirements for operation down to -40°C , which is frequently encountered during the Canadian winter. The most widely used primary couple is lithium-sulphur dioxide, although high rate lithium-manganese dioxide batteries have recently been developed as a possible replacement.

During the last decade, there were two new rechargeable systems that became widely used: nickel-metal hydride and lithium-ion. These have replaced nickel-cadmium (nicad) in some cases, but they are not as robust as nicad and do not have such good low temperature performance. Their main benefit is that they have a higher energy density, so that the batteries have a longer service life. Lithium-ion batteries have proven to be commercially successful for consumer electronics and are now entering military service. However, the chemistry of the cells is still evolving and the batteries need to be well

designed in order to remain safe throughout their projected cycle life.

For the purposes of this study, only commercially manufactured cells have been considered that are likely to be employed by the Canadian and U.S. forces in batteries for communications systems or weaponry. All of the batteries discussed contain high-rate cells, which are spirally wound in the case of cylindrical cells and contain multiple folds in the case of flat format cells. Details of the different battery couples can be found in Linden and Reddy, 2002.

2. PRIMARY BATTERIES

For the last two decades, the chemistry of choice for portable primary batteries has been lithium-sulphur dioxide. Because this system is pressurised (about 3 atmospheres of sulphur dioxide) and, very rarely, cells have been known to vent violently, there has been a push to replace this chemistry with lithium-manganese dioxide. The latter couple has a higher energy density (so standard military batteries have a higher amp-hour capacity), but it does not have useful capacity at -40°C . Also, when the latter system vents, it is much more likely to cause a fire than lithium-sulphur dioxide (the sulphur dioxide itself will suppress a fire just as carbon dioxide does). It should be noted that the lithium-sulphur dioxide cells incorporate a machined pressure vent that is activated when the cell temperature is approximately 95°C , while the lithium-manganese dioxide cells have a vent that is activated at $140-150^{\circ}\text{C}$. The two systems have their pros and cons. Both types of battery are in service with U.S. and Canadian forces, but the user needs to remember that the lithium-manganese dioxide

batteries are not for use at low temperatures. There are other battery chemistries available, such as lithium-thionyl chloride. This couple is high energy density and has good low temperature performance; however, the batteries have safety issues for military application, which will be discussed later.

2.1 PERFORMANCE

Figure 1 compares the performance of three different types of BA-521 and BB-521 batteries at different temperatures. These batteries are used by the CF for a hand held radio and they have been discharged according to the radio's duty cycle for transmission, receive and standby using 944 mA (10 sec) : 60 mA (10 sec) : 27 mA (80 sec), with 8.0V as the cut-off voltage. The battery voltage drops (polarises) when the current increases, which is partly due to the kinetics of the electrochemical reactions and partly due to the intrinsic resistance inside the cells. It can be seen that the lithium-manganese battery is at the edge of its performance for TX at -20°C and that at -10°C the TX pulse is always close to the 8.0V cut-off. The battery polarisation during the TX pulse can be seen to steadily increase as the discharge temperature falls. The sulphur dioxide batteries are clearly better for use below -10°C : they yield 45% of their room temperature operating time at -30°C and 25% at -40°C . Minus 40°C is seen to be at the edge of operation for TX pulses, although these batteries do work at -50°C with lower discharge rates.

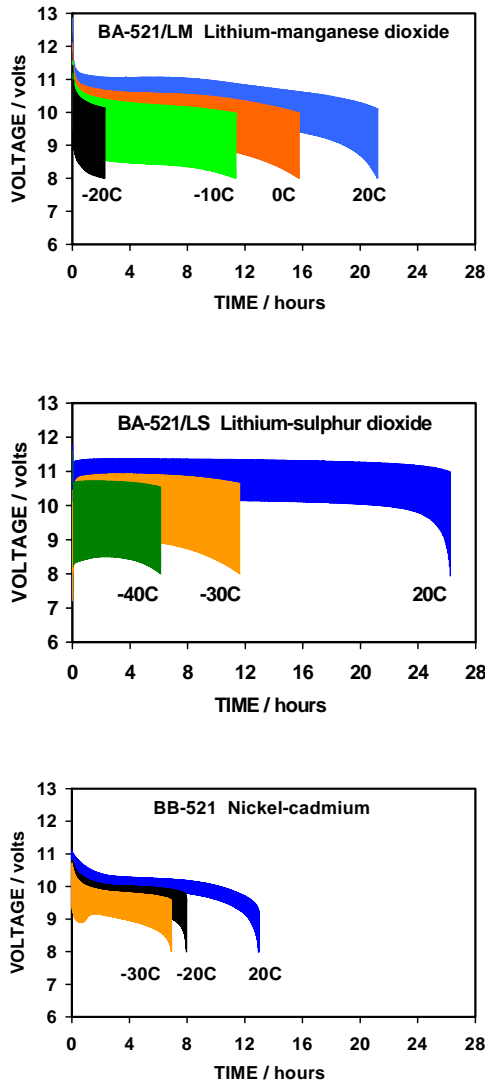


Figure 1. A comparison of the voltage-time profiles, obtained at different temperatures, of three versions of the same size primary and rechargeable battery (it should be noted that the cells present in the BA-521/LS battery were slightly larger than those in the other two batteries, so its discharge time at room temperature is still longer than that of the BA-521/LM).

The rechargeable nickel-cadmium BB-521 battery is also shown in Fig. 1. Rechargeable batteries always have a lower capacity than their primary counterparts because the electrodes need to remain intact for recharging, so a substrate is needed, which leads to extra weight and volume. The operating time at room temperature can be seen to be half that of the primary batteries, but the polarisation is a lot lower. The latter is because nicad is an aqueous system and so the electrolyte is more conducting than the non-aqueous electrolytes that are present in the primary batteries. Figure 1 also shows that the nicad battery has better performance than the BA-521/LM battery at low temperature.

2.2 SAFETY

In the field there is the possibility of a battery being penetrated by a bullet, so it is important to know how the battery is likely to behave when it is in close proximity to, or being carried by, the soldier. In the laboratory environment we use steel nails in place of bullets. When the nails are shot into a cell, they remain in place, causing a severe, internal short-circuit. This causes a rapid rise in temperature, especially in the immediate vicinity of the nail and any inflammable material may ignite.

In the following experiments, a 0.22 calibre Remington nail gun was used to shoot 2.5" x 0.125" nails into the cells and batteries. The nail gun was held in a steel jig above the target. Single cells were taped to thick pieces of plywood, which served to hold them in place and to decelerate the nails, so that they remained embedded in the cells and maintained the short-circuit. Voltages and temperatures were monitored using a data-acquisition and control unit, scanning every second. Cell temperatures were measured using two thermocouples taped along the cylinder, either side of the middle, which was the target for the nail. The thermocouples were for guidance only, because they were placed away from the target area and only measured the surface temperature of the cells: the internal temperatures were probably appreciably higher. The nail gun was triggered using a long rod, so that the operator was not too close to the cells. Face shields and a shatterproof glass shield were used for safety.

Nail penetration was first carried out on D-size lithium-sulphur dioxide cells. With these, the external temperature reached 80°C but the cells did not behave dangerously. Sulphur dioxide could be smelled when the nail first penetrated the cell. Because sulphur dioxide is electrochemically reduced during the cell discharge reaction, loss of the gas also means that the cell is losing its energy content and becoming less potentially hazardous. Nails were also fired into BA5590 batteries (these batteries contain two strings of five D-size cells each that can be joined together in series or in parallel) such that they passed through 2 of the D-size cells but, again, no hazardous event occurred. The nail gun was lined-up with the cells through the use of an x-ray image of the battery and, after the test, the position of the nail was confirmed by a further x-ray. A typical image is shown in Fig. 2.

Lithium-manganese dioxide cells contain highly inflammable ether solvents (typically a mixture containing 1,2 dimethoxyethane), which can ignite during abuse. At the same time, manganese dioxide is an oxidising agent and it decomposes at 535°C, giving off oxygen, thus adding to the intensity of a fire. The early D-size spirally wound versions of these cells frequently proved to be hazardous under electrical and physical abuse e.g. they could vent violently with fire when subjected to an external short circuit. More recently, the polypropylene separator in these cells has been replaced by a complex three-

layer design consisting of polypropylene / polyethylene / polypropylene, or by a polypropylene separator coated with wax. These are described as shut-down separators. In the former case, the polyethylene begins to-melt at around 135°C and the micropores in the separator close up. In the latter case, the wax melts at a similar temperature and blocks the pores of the polypropylene. This prevents the flow of ions through the separator, shutting down the discharge. This happens well in advance of the melting point of lithium metal (180°C), which is the trigger for violent reaction.

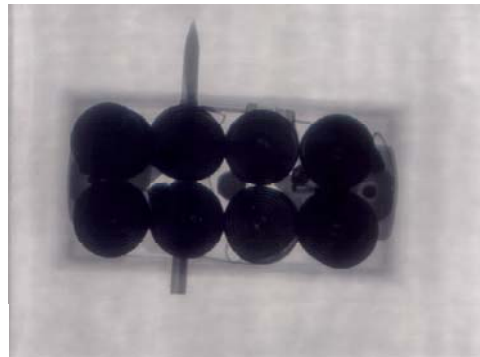


Figure 2. X-ray photograph of a BA521/LS battery containing eight A-size lithium-sulphur dioxide cells, plus a nail.

Nail penetration was carried out on state-of-the-art D-size lithium-manganese dioxide cells, with no hazardous events. The external temperature of the cells rose to 95°C, but there was no fire. The shutdown separator will have been activated in the regions close to the nail and further away as the heat was transferred by the metal electrode and mesh support. It is believed that the shutdown separator reduces the short-circuit current to the extent that the flash-point of the electrolyte solvent is never reached. Nail penetration was also carried out on a BA-5390 (the lithium-manganese dioxide equivalent of a BA-5590). A nail was first shot into 2 cells in one string and no hazardous event resulted. A second nail was then shot into 2 cells of the second string and, again, there was no hazardous event. Therefore, state-of-the-art D-size lithium-manganese dioxide cells were found to be safe with respect to nail penetration. However, there have been isolated incidents of batteries catching fire during environmental testing and discharging, so there are still some issues that are being resolved.

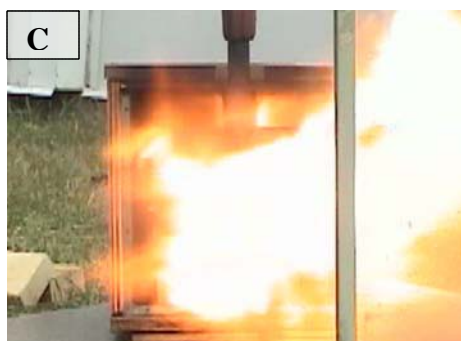


Figure 3. A. Photograph of a BA-521 battery; B. a lithium-thionyl chloride version of the battery in the nail test apparatus. C. the battery exploding (see text). D. the damaged apparatus.

A prototype BA-521, which contained lithium-thionyl chloride cells was offered to the CF for evaluation. This couple has very good low temperature performance but there are safety issues with the spirally wound cells. A nail test was performed on this prototype battery and it immediately caught fire and emitted thick white choking fumes of hydrogen chloride (hydrochloric acid). The fire was put out but, 5 minutes later the battery exploded violently, severely damaging the nail test apparatus (see Fig. 3). What had happened here was that the nail had penetrated 2 or 3 cells of one of the 4-cell strings of the battery, while the other string was left undamaged. However, the heat generated by the short-circuit had eventually been conducted to the good cells and, when the melting point of lithium metal had been reached, these cells reacted violently. This is an important aspect to remember when encountering a vented or damaged battery in the field – some of the cells may still be live and plastic insulation on the cells and connecting wires may have been burned away such that a short-circuit could be activated by disturbing the battery.

Very recently, flat format versions of the lithium-manganese dioxide cells and batteries have been developed (e.g. Matthews and Naukam, 2002). These are contained in an aluminised plastic pouch (hence the name pouch cells) and the cells can be stacked to make a battery with no void space, unlike with cylindrical cells. Although at first sight the pouch cells might be thought of as more dangerous than metal can cells, the logic is that, if a pouch cell gets too hot because of a fault, the plastic pouch will leak before a dangerously high pressure or temperature is reached. Hence the inflammable solvent may leak and disperse without fire. At the present time, our laboratory has not carried out any testing with these cells, though.

In summary, the choice of high energy density, high rate, primary cells for portable batteries lies between lithium-sulphur dioxide and lithium-manganese dioxide. The former are lower energy density at room temperature but have better performance below -20°C . They will release a toxic gas when they vent, although there is usually no fire. Venting is not a big problem outdoors but can be in a confined space. Venting can occasionally be violent and injure personnel. Venting of lithium-manganese dioxide cells is less violent than for lithium-sulphur dioxide, but the vented solvent could cause a fire, which might

then spread to other cells or equipment. Shutdown separators have reduced the risk of a fire, but not completely eliminated it.

3. RECHARGEABLE BATTERIES

The commonly used portable rechargeable battery has traditionally been nickel-cadmium, but the dominance of this couple is now being challenged by nickel-metal hydride and lithium-ion. Nickel-metal hydride batteries have the same voltage as nicad, 1.2V, but the cells have a higher energy density, and have approximately 40% more amp-hour capacity. As is usually the case with a new system, there are drawbacks. Nickel-metal hydride cells are less robust and have a shorter cycle life. One reason for the shorter cycle life is that the cells become hotter during charging and that the metal hydride is irreversibly damaged by the heat. The higher temperatures originate from the recharge reaction, which is endothermic for nicad but exothermic for nickel-metal hydride. Therefore, nickel-metal hydride cells are more prone to damage from overcharging than nicad and charging needs to be terminated earlier. For this reason, nickel-metal hydride military batteries usually contain thermistors for monitoring the cell temperatures through external contacts that interface with the battery charger. The charger can then terminate charging when a particular temperature is reached. Nickel-metal hydride cells have been described as a stopgap couple that will be replaced by lithium-ion. However, the performance of this couple has been steadily improving, so it should remain an important system for many years. Although lithium-ion cells do have a slightly higher energy density, it should be remembered that they also contain an organic solvent electrolyte and, therefore, are more inflammable than the two aqueous nickel couples.

Although nicad batteries are unlikely to catch fire themselves, they can still cause a fire through poor battery design, whereby an internal cell-to-cell short circuit can lead to the intercell connectors becoming red hot and melting the battery case, then starting a fire. Such an incident occurred several years ago on a Canadian commercial airliner, when a camcorder battery suddenly started to smoke in the pouch at the back of an airline seat. Luckily the smoke was quickly suppressed but, had the battery been inside the luggage hold, there could have been a

fire. The battery in question only contained five AA-size cells and 4 of these cells were shorted by a long metal ribbon that went from one end of the battery array to the other. The safety device that was meant to shut down the battery, because of a high current or temperature, was attached to the side of the fifth cell, which was not involved in the short-circuit. The incident was the result of poor battery design. The battery was, in fact, a generic version of the original. With respect to nail penetration, the two nickel couples do not catch fire and their main problem is emission of a very small amount of hot alkaline electrolyte. Therefore, these will not be discussed further.

The first commercially produced lithium rechargeable batteries had a lithium metal negative electrode and a molybdenum sulphide positive electrode. Lithium ions were intercalated inside the molybdenum sulphide during discharging and lithium metal was replated during charging. It is well known to researchers that it is difficult to repetitively replate lithium metal without producing the occasional small whisker of metal (called a dendrite) that can grow across from the negative electrode and eventually short out to the positive electrode. Although only a small amount of lithium may be involved, the dendrite can melt when the short-circuit is formed and then create a violent chemical reaction. The company that marketed these batteries terminated production following an incident in which a cellular phone battery caught fire. Since then, research has concentrated on lithium-ion systems, in which the negative electrode is a carbon material that intercalates the lithium as ions, so that no metallic lithium is present.

3.1 LITHIUM-ION BATTERIES

The majority of lithium-ion batteries that are in service use lithiated cobalt oxide as the positive electrode material. These batteries have proven to be safe in domestic and commercial applications, although it is well documented that they can vent and catch fire if they are overcharged (Lampe-Onerud et al, 1999). The safety of these batteries relies upon embedded electronics protecting each cell individually. The cell discharge limit is set at around 2.75V and going below this limit will lead to an irreversible loss of capacity, but no safety problems. The cell charging limit is usually set to 4.2V. At voltages above this value, the cells can eventually undergo thermal runaway due to decomposition of the cobalt oxide. For a cell

charged to 4.2V, the onset temperature for thermal runaway is approximately 80°C and the cell will become hazardous after around 18 hours at that temperature. With a cell charged to 4.8V, the onset temperature is only 40°C and the cell becomes hazardous in only 7 hours. Consequently, it is very important that these cells not be overcharged. In the case of a battery pack, it also means that each cell needs to be monitored individually, because cell capacities do not always degrade evenly with time, so a lower capacity cell in a battery pack can become overcharged.

Lithium-ion batteries are much safer than the earlier lithium metal rechargeable batteries, because of the lack of lithium metal; however, it is still possible to deposit lithium metal if the recharge rate is too high, such that lithium ions arrive at the negative electrode at a faster rate than they can diffuse into the carbon material. A lithium-ion version of the BB-590 battery is now becoming available, which is designated the BB-2590/U. This battery has a nominal capacity of 4.2 Ah and can contain twenty-four 18650 cells or eight fat-D size cells. At the present time we have only carried out a nail test on a state-of-the-art 18650 cell and it did not behave hazardously. This was probably due to the incorporation of a shutdown separator in the cell.

The standard commercially available lithium-ion cells are not suitable for Canadian military service because they have very poor performance at temperatures below -10°C. This is because cell manufacturers are aiming at the consumer portable electronics market. However, during the past few years, electrolytes have been developed that yield good performance down to -30°C and limited performance at -40°C (Ein-Eli et al, 1998). Batteries containing these electrolytes are likely to enter service in the near future.

3.2 LITHIUM-ION POLYMER CELLS

Lithium-ion cells are also being developed in a flat format that uses a polymer electrolyte. There are two types of polymer electrolyte battery: the first is a true all solid state version that uses an ion-conducting polymer as the electrolyte; then there is a gel-polymer version, in which the liquid electrolyte is trapped inside the micropores of a polymer and so only appears to be solid. It is this latter version that is of interest to the military because the electrolyte

conductivity is much higher at reduced temperatures than the all-solid state version. The gel-polymer cells are packaged inside an aluminised plastic pouch and the electrode materials are the same as for regular lithium-ion cells. Several companies are developing these cells for commercial and military application, including versions containing electrolyte for low temperature operation.

Figure 4 compares the voltage-time discharge curves of lithium-ion gel-polymer cells that contain the standard electrolyte with those of a low temperature version. The curves include discharges at various temperatures and it is clear that the low-temperature version of the electrolyte has a much better performance at -20°C and below. The cycle life has been found to be suitable for military use, by exceeding 200 full discharge cycles during cycling at multiple temperatures, so safety is the next issue. Because the cells are contained in a plastic bag, they behave differently from the metal can versions.

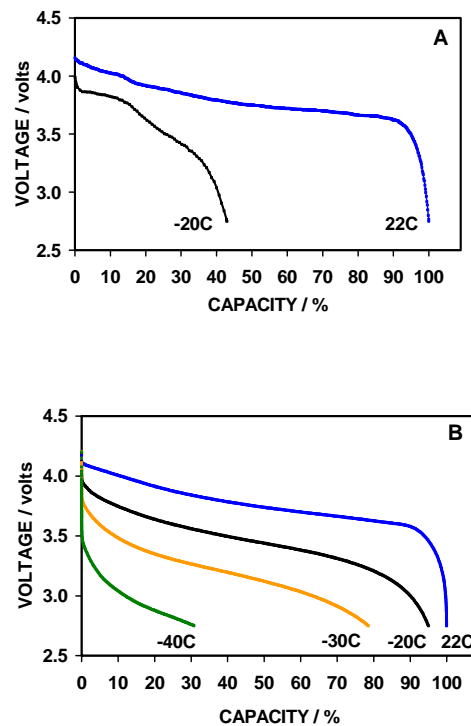


Figure 4. A. shows the discharge performance of a lithium-ion gel-polymer cell at -20°C in comparison with that obtained at room temperature. B. shows the discharge curves, at different temperatures, of cells containing a modified electrolyte, formulated to have good low temperature operation.

We have carried out some severe electrical and physical abuse tests on lithium-ion gel-polymer cells. Electrical testing has included short circuit and forced overcharging, while physical testing has included impact testing with a heavy weight, hitting the cell with a hammer, slicing the cell with an axe, and nail penetration. In most of these tests the cells were free standing while, in some, the cells were constrained by a thick plastic cover in order to simulate cells inside a battery case (this prevented the plastic pouch from puffing up due to internal pressure).

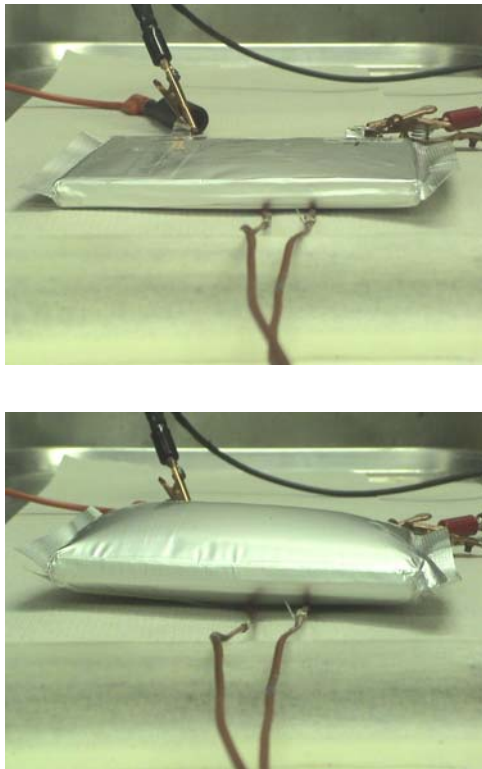


Figure 5 compares the state of a lithium-ion gel-polymer cell before (top) and after (bottom) prolonged overcharging, at twice the recommended charging current, for 24 hours (voltage limited to 8.4V). The cell swelled badly but did not rupture.

Figure 5 shows what happened to a cell during overcharging. The standard procedure is to overcharge using twice the recommended current, with the voltage limited to twice the normal charging cut-off voltage. The electrode-electrolyte structure was completely destroyed by this procedure, but the cell pouch remained intact. The maximum temperature measured was 55°C. The cells were also found to be safe under short-circuit. This is because these cells only support a

relatively low current density under normal use. For example, a 10 Ah test cell delivered around 60A for 20 seconds, before the current fell rapidly to less than 10A. The maximum temperature attained was 60°C.

The UN impact test, which was really designed for metal can cells, requires having a 5/8" diameter rod resting across the cell and then dropping a 20 lb weight onto it from a height of 2'. The UN tests are aimed at the safety of new cells during transportation from the factory, which is often by air. For these tests, the cells need only be 50% charged, because new cells are delivered with a low state-of-charge. For our testing, we used 100% charged cells, because we are considering the safety of the cells in service. With this test, impact caused a rapid increase in pressure in the cell and it ruptured within 3 seconds, emitting copious white fumes. The cell then caught fire. When the test was repeated using a 50% charged cell, it was found to be passive. A perhaps more realistic impact test that we used was to hit the cell with a small hammer. This was done several times on the same fully charged cell and it maintained its voltage of 4.2V and did not increase in temperature. The indentations on a cell can be seen in Fig. 6. Another fully charged cell was chopped with an axe as it lay flat. The cut was in between the two cell tabs and across half of the cell. The cell maintained its voltage and no smoke or fire was produced. The test was terminated after 20 minutes.

Nail penetration of fully charged cells was carried out using a long metal rod with a hollow tip to push the nail into the cell from a distance. With a freestanding cell, there was an immediate increase in pressure and the cell ruptured and later caught fire. It was also found that the cells could be caused to short-circuit and emit copious white fumes by stabbing them with a ballpoint pen. Therefore, these cells are very sensitive to impact by sharp objects, as opposed to blunt objects. However, when a 50% charged cell was subjected to nail penetration, it was safe; there was no expansion of the pouch due to an increase in internal pressure and the temperature remained relatively low. Nail penetration was also carried out on pouch cells that were constrained, in order to simulate what could happen with cells inside a battery case. For these tests, a wooden base was used, and a 0.09" thick sheet of clear plastic (Lexan) was screwed into the wood to hold the cell down, with silicone used as a sealant. The set-up can be seen in Fig. 7. With nail penetration,



Figure 6. Photograph showing damage inflicted onto a lithium-ion gel-polymer cell by several hammer blows.



Figure 7. Nail penetration of a lithium-ion gel-polymer cell constrained under a 0.09" sheet of Lexan plastic. Top: 1 second after penetration. Bottom: 3 seconds later.

there was a large build-up of pressure and the nail was ejected from the cell along with large amounts of white fumes mixed with black particles. However, the cell did not catch fire in this case.

In summary, lithium-ion gel-polymer pouch cells appear to be safe with electrical abuse but the fully charged cells are unsafe upon penetration by a sharp object or from a severe impact. Therefore, a hard battery case is required to protect the cells. It should be possible to increase the safety of these cells by the use of shutdown separators and flame-retardants. However, the cobalt oxide itself is also a problem because of its low decomposition temperature, whereby oxygen is emitted. For this reason, alternative positive electrode materials are being investigated by many organisations, such as lithium manganese dioxide spinel and lithium iron phosphate

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CONCLUSIONS

For operation down to -40°C, lithium-sulphur dioxide is still the best primary battery couple for portable equipment. Lithium-sulphur dioxide and lithium-manganese dioxide batteries have similar levels of safety: both are relatively passive to nail penetration. For rechargeable batteries, nickel-metal hydride and regular format lithium-ion cells are also safe to nail penetration. New electrolytes are leading to better low temperature performance for lithium-ion and also for lithium-ion gel-polymer cells. The latter cells were found to be reactive to nail penetration and to heavy impact, when in the charged state, and so need to be protected by a hard battery case.