Safety Characterization of Li/MnO₂ Cells
Li/MnO₂ cells are designed to avoid cell venting providing an advantage over Li/SO₂ Cells

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ABSTRACT
The following paper provides an overview of the Ultralife Batteries, Inc. and Ultralife Batteries (UK) Ltd. cell design and component selection utilized in the manufacturing of lithium-manganese dioxide (Li/MnO₂) cells. A limited comparison of Li/MnO₂ to lithium-sulfur dioxide (Li/SO₂) cells is presented focusing on each cell’s performance characteristics under abuse conditions. These characteristics indicate that Li/MnO₂ cells may be used safely in applications where Li/SO₂ cells may be considered inappropriate. The Li/MnO₂ cells essentially have an additional safety feature that is not present in Li/SO₂ cells. Shutdown separator provides this additional feature. This information is important to end users so that proper decisions can be made about the applicability of using Li/MnO₂ cells in applications that can benefit from their inherent safety over Li/SO₂ and/or by the performance benefit over alternative chemistries in demanding applications. Applications in enclosed areas that may reach high storage and operating temperatures are especially appropriate for the Li/MnO₂ cells in comparison to Li/SO₂ cells.

Selected Cell Design Detail
Incorporated into the many considerations in the design of Li/MnO₂ cylindrical cells is appropriate insulation separation between anode and cathode and, as determined by Ultralife Batteries, it is essential to use a shutdown separator in Li/MnO₂ cells.

Shutdown separator, consisting of polyethylene sandwiched by two outer layers of polypropylene film, still provides rapid and efficient transfer of ions (similar to non-shutdown separators) from the anode to the cathode due to its integral porous nature and thin structure. Shutdown separator works based on the melting point of polyethylene. The polyethylene will melt when it reaches approximately 132°C and close off its porous structure. The polypropylene remains intact. The separator physically remains in place and minimizes the available locations for ionic transfer to occur. Shutdown separator has proven itself for both performance and safety. Specifically, it has been established as a major factor in the predictable performance of Li/MnO₂ cells under abuse conditions due to its excellent shutdown characteristics at the specific temperatures required.

The use of shutdown separator provides a tremendous advantage over lithium cells without this feature. The ability of the Li/MnO₂ cells to shutdown and not vent when subjected to short circuit at room temperature, and even at elevated temperature of 55°C, has been accomplished.

Anode construction includes a lithium foil with an appropriately sized copper inlay to serve as a current collector and as a cell reversal protection feature. In conditions of forced discharge, the copper will plate to the cathode and form a safe, low resistance current bridge. This bridge prevents lithium plating and the overheating that would accompany it, as well as the potential catastrophic events associated with sending all of the cell current through a small lithium bridge.

Li/MnO₂ cells are filled with solvent-based electrolyte that is a liquid at room temperature and standard pressure. Using a vacuum fill technique to reduce the cycle time required to accomplish the filling operation, the filling is completed without cell pressurization.

By contrast, Li/SO₂ cells are filled under pressure, as this is required to keep the SO₂ in a liquid state. The filling pressure is typically in the range of 40 – 50 psi at room temperature, which is the vapor pressure of SO₂.
Cell Containment

Both Li/MnO$_2$ and Li/SO$_2$ cylindrical cells can use the same type of canister. Containment of Li/MnO$_2$ cells is accomplished through the use of nickel-plated cold rolled steel or stainless steel cans. These cans may have a vent feature formed into them or may have a discrete low-pressure vent that can be designed to activate at predetermined internal cell pressures. Vents typically have been patented or are company proprietary due to their custom designs.

Additionally, Li/MnO$_2$ cells may also be packaged in container types other than cylindrical cans when shutdown separator is utilized. Specifically, Ultralife Batteries use two others; they are a flexible (soft-pack) laminated foil package container and a plastic injection molded container.

The flexible (soft-pack) foil package container may be utilized because no cell pressurization occurs over the range of operation or storage temperatures. The flexible material is a multi-layer laminate, consisting of aluminum foil between layers of polypropylene or polyethylene. These foil-packaged cells are actually sealed under vacuum, and do not lose their vacuum condition unless the package is compromised or subjected to abusive high temperature conditions. Under these conditions, the foil cell will expand because the internal pressure, caused primarily by the vapor pressure of the solvent, exceeds atmospheric pressure.

The plastic injection molded container is made of glass filled polypropylene and utilizes an outer metal jacket sleeve or metallic label to minimize moisture ingress and solvent egress. This product utilizes a custom Ultralife patented shutdown separator assembly, so effective that the plastic container utilized for this consumer product does not have a vent. This unique capability is illustrated in Figure 1, where the maximum capability is below 80°C.

Cell Venting

In both the Li/MnO$_2$ and Li/SO$_2$ steel-canister cells, a vent is necessary for the prevention of a catastrophic event, namely unpredictable behavior including the possibility of explosion when the cells are exposed to abuse conditions. Vents in Li/MnO$_2$ cells have somewhat of a different purpose than in Li/SO$_2$ cells.

Differences between the chemistries are highlighted with the short circuit abuse condition. In the case of Li/SO$_2$ cells, the purpose of a vent is to provide a short circuit safety outlet for the pressure that builds up as a result of the heat generated during the short circuit. If the vent were impeded to prevent operation, the cell internal pressure would build to a point where explosion is likely.

The short circuit behavior of Li/MnO$_2$ cells, when constructed with shutdown separator, includes temperature rise, internal pressure increase and shutdown separator activation, but does not rely upon vent operation. The vent does not need to activate because the cell temperature decreases upon the shutdown separator operation, which in turn causes the cell pressure to decrease. This shutdown process continues until the cell is inoperative due to no available ionic path or no available active material remaining.

If the shutdown separator fails to perform adequately, (for example in the case of extreme abuse conditions above 130°C), the vent will operate before the cell reaches 150°C, due to the increase in pressure associated with the increasing temperature in the cell, well below the melting point of lithium, (180°C). Therefore the Li/MnO$_2$ cell has a redundant safety feature in a short circuit condition.

Fig. 1 Ultralife Batteries U9VL-J Li/MnO$_2$ three cell 9-volt battery temperature and current curves during ambient temperature short circuit test.
At elevated temperature the cell behavior is similar, except the pressures are reached faster because the starting point temperature is higher. It has been shown that Li/MnO$_2$ cells still will not vent even when shorted at 55°C.

Li/SO$_2$ cells cannot take advantage of the shutdown separator because these cells will, by design, have already vented when they reach 110°C due to the pressure reached by the SO$_2$ at this temperature. Comparatively, the shutdown separator in a Li/MnO$_2$ cell activates at approximately 132°C.

Typical cell vent activation pressures used by Ultralife are dependent on cell construction. Currently the Ultralife HiRate™ cylindrical cells use a burst disc design that has a vent activation range of 220 - 260 psi. Additionally, Ultralife has developed a formed-can vent that activates in the range of 350 - 450 psi.

For comparison, Li/SO$_2$ cans have a vent range of 350 - 500 psi, and typically have an internal pressure range of approximately 40 to 50 psi at room temperature, with the pressure reaching 100 to 150 psi at 55°C.

Table 1. Cell Activation Temperatures and Pressures compared to Shutdown Separator Activation Temperature and Lithium M.P.

<table>
<thead>
<tr>
<th>Cell Type / Material</th>
<th>Temp</th>
<th>Press</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(psi)</td>
</tr>
<tr>
<td>Li/SO$_2$ Formed Vent</td>
<td>100-110</td>
<td>350-500</td>
</tr>
<tr>
<td>Shutdown Separator</td>
<td>132</td>
<td>-</td>
</tr>
<tr>
<td>Li/MnO$_2$ Burst Disc</td>
<td>140-150</td>
<td>220-260</td>
</tr>
<tr>
<td>Li/MnO$_2$ Formed Vent</td>
<td>140-150</td>
<td>350-450</td>
</tr>
<tr>
<td>Lithium Melting Point</td>
<td>180</td>
<td>-</td>
</tr>
</tbody>
</table>

Battery Considerations

A Thermal Cut-Off device (TCO) must be included in battery designs using Li/SO$_2$ cells to prevent venting. This device, typically rated to activate at 93°C, is required because of the relatively low vent temperature of Li/SO$_2$ cells of 100 - 110°C.

The thermal management of Li/MnO$_2$ batteries does not always call for a TCO due to the lower rate of temperature increase on discharge compared to Li/SO$_2$, especially at elevated temperatures.

Safety Feature Characterization

Li/SH$_2$ cells vent SH$_2$ gas under relatively high pressure. The rapid release of the expanding gas causes a cooling effect on the cells.

By contrast, Li/MnO$_2$ cells are much less likely to vent unless under excessively abusive conditions. For example, short circuit at temperatures above 55°C, or long term storage at temperatures above 85°C.

Cells are routinely stored at 90°C for 2 hours without venting, and then vented safely within 2 hours when the temperature is raised to 150°C, as required by certain military specifications.

Toxicity

Although Li/MnO$_2$ cells upon venting may emit flammable vaporized solvents and gases, the material is non-toxic.

In comparison, the Li/SH$_2$ cell upon venting emits SO$_2$ gas, which is not flammable but is extremely toxic, noxious and corrosive.

Disposal

Ultralife Batteries has developed a simple technique to de-activate cells.

Cells for disposal have their vent activated and are placed in a tank partially filled with saltwater solution to allow the lithium to react extremely slowly with the water until completely dissolved.

The principle of this practice allows for the expulsion of the H$_2$ gas that is formed upon the reaction of lithium and H$_2$O, and limits the H$_2$O ingress into the cell, allowing a controlled reaction to occur. The tank of saltwater solution dissipates the heat generated by the reaction and the container is well-ventilated out of doors to remove the possibility of build-up of generated gas. On the complete dissolution of lithium in the cells, the tanks are removed to certified disposal sites.

Applications

Li/MnO$_2$ cells clearly provide an advantage over Li/SH$_2$ cells when considered for applications such as in a contained environment. Limited air exchange locations, such as commercial airplane cabins and automobiles are prime examples.
Even with batteries mounted outside of the automobile passenger compartment, it is possible for vented SO$_2$ gas to rapidly ingress to the compartment, and cause excessive levels to be reached in a short period of time. Breathing will become quickly affected.

Another application is military airplane cockpits. Although air supply is typically controlled, the extremely limited volume of the cockpit could cause high concentrations of vented SO$_2$ gas to accumulate rapidly.

**Approval Recognition**

Both the Ultralife U9VL-J battery produced for consumer and commercial use applications, and the Ultralife HiRate™ cells have UL component recognition, having met the requirements of UL Standard 1642.

**Conclusion**

The exclusive use of shutdown separators by Ultralife in its Li/MnO$_2$ cells provides numerous advantages over cells without this feature. This prevents venting in a short circuit condition, a characteristic not possible with Li/SO$_2$ cells, which can vent when shorted.

**Acknowledgment**