Program Development

Lithium Battery Safety

A look at Woods Hole Oceanographic Institution's program

By Ronald H. Reif, Mark Liffers, Ned Forrester and Ken Peal

WOODS HOLE OCEANOGRAPHIC INSTITUTION (WHOI) uses primary and secondary lithium batteries in a variety of oceanographic research applications. Primary (nonrechargeable) lithium batteries generally contain lithium metal, while most secondary (rechargeable) lithium batteries contain an ionic form of lithium (lithium-ion). Because lithium batteries contain more energy per unit weight or a relatively higher energy density than conventional batteries, they have become popular and widely used in various applications. The same properties that result in a high energy density, however, also contribute to potential hazards if the energy is released at a fast, uncontrolled rate.

Multiple external and internal events involving primary and secondary lithium batteries (including hot cells, fires, ruptured cells and leaking cells) prompted WHOI to develop and implement a comprehensive lithium battery safety program. This article describes lithium batteries and applications, hazards, controls, key elements of a comprehensive safety program, emergency procedures, waste management and transportation requirements.

Lithium Batteries & Applications

Primary lithium batteries have lithium metal or lithium compounds as an anode. Many different lithium battery chemistries are suitable for a variety of operating conditions. Advantages of lithium batteries compared to alkaline batteries include lower weight, extended shelf life, higher capacity (as measured in ampere-hours, Ah), higher energy density (as measured in watt-hours per unit weight, Wh/g) and lower cost per capacity.

The Ah rating or capacity is a common battery rating that is the maximum sustained amperage drawn from a fully charged battery over a certain time (e.g., 20 hours) to a point where the battery is at 100% depth of discharge. Energy density is a ratio of the capacity of a battery to weight (Ah/g). Sometimes, energy density is expressed as capacity per unit volume of a battery, Ah/cm^3. Batteries also can be rated in energy output if their average voltage during discharge is known. Energy output is determined by multiplying capacity and voltage with units of watt-hours (Wh).

Secondary or lithium-ion (Li-ion) batteries, not to be confused with primary lithium batteries, do not contain metallic lithium. Li-ion batteries are rechargeable batteries containing lithium intercalation anode materials, where the lithium ion moves from the anode to the cathode during discharge and from the cathode to the anode when charging. Advantages of Li-ion batteries when compared to equivalent rechargeable batteries include higher energy density, higher output voltage, lighter weight, no memory effect, low self-discharge rate and faster charge rates; in addition, they do not contain highly toxic metals such as nickel, cadmium, lead and mercury.

Lithium batteries can be used in place of ordinary alkaline cells in many devices. Although more costly initially, lithium cells provide much longer life, thereby minimizing battery replacement. Lithium batteries find application in many long-life, critical devices, such as artificial pacemakers and other implantable electronic medical devices. Small lithium batteries are commonly used in small, portable electronic devices, such as watches, digital cameras, remote car starters and calculators, and as backup batteries in computers and communication equipment.

Li-ion batteries are common in portable consumer electronics, such as cell phones and laptop computers, because of their high energy-to-weight ratios, lack of memory effect and relatively slow loss of charge when not in use. In addition to consumer electronics, Li-ion batteries are increasingly used in defense, automotive, aerospace and research applications due to their high energy density.

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WHOI uses both primary lithium batteries and Li-ion batteries in various applications. One application example for Li-ion batteries is the remote environmental monitoring units (REMUS), a type of autonomous underwater vehicle (AUV). AUVs are robotic submarines that navigate at 3 to 5 knots without being operated by a human crew. They are used for both scientific research and military operations, such as locating mines.

There are several versions of REMUS. The REMUS-100 uses four 250 Wh battery modules each containing 14 Li-ion cells that are arranged as 7 in series and 2 in parallel, yielding a nominal output of 26 V and a total energy of 1,000 Wh. The REMUS-6000, which operates to 6,000 m depth, is loaded with a pair of 5.5 kWh rechargeable Li-ion battery assemblies containing a total of 16 battery modules each providing 690 Wh. Photo 1 shows the REMUS-100 Li-ion battery assembly and Photo 2 shows a pair of REMUS-6000 battery assemblies.

An application example of primary lithium batteries is ocean bottom seismographs (OBS), which are ocean floor seismic-monitoring instruments. OBS measure both earthquake-generated seismic waves and artificial sources. Two types of OBS are operated at WHOI: short-deployment and long-deployment. Short-deployment OBS are relatively small and light for easy deployment and recovery. With a 6-month battery capacity, they are designed for relatively short-term experiments and record high frequency earth motions.

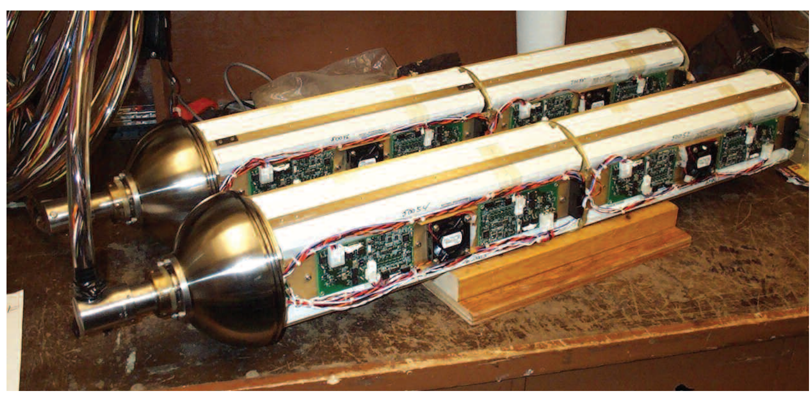
Long-deployment OBS can be deployed for a year or more to record earth motions. Four orange fiberglass "hardhats" that are mounted on a plastic grillwork contain primary lithium batteries and electronics. A differential pressure gauge measures earthquake-generated waves in the water. The seismometer sensor is housed in a metal sphere suspended by a corrodible link. When an OBS is deployed, the link corrodes, positioning the seismometer on the seafloor.

The primary lithium batteries used to power various OBS components include lithium sulfuryl chloride cells and lithium thionyl chloride cells. Complete packs for each OBS typically require between 100 and 150 lithium battery cells. These are D and double D-sized cells with a rated voltage of 3.6 to 3.9 V and rated cell capacities of 15 to 35 Ah. Photo 3 shows opened glass spheres with a) part of the battery pack and b) the electronics. Photo 4 shows the long deployment OBS.

Lithium Battery Hazards

From 2004 to 2008, WHOI experienced multiple incidents involving primary lithium batteries. These included off-gassing cells, leaking cells, hot cells and a fire/explosion. A November 2005 event involved a fire and subsequent explosion of an OBS that had been deployed offshore near Puerto Rico. The fire occurred aboard a research vessel approximately 30 hours after recovery from the ocean and during the data offloading phase. Fortunately, no injuries occurred.

Photo 1 (top) shows a REMUS-100 Li-ion battery assembly while Photo 2 (middle) shows a pair of REMUS-6000 battery assemblies.



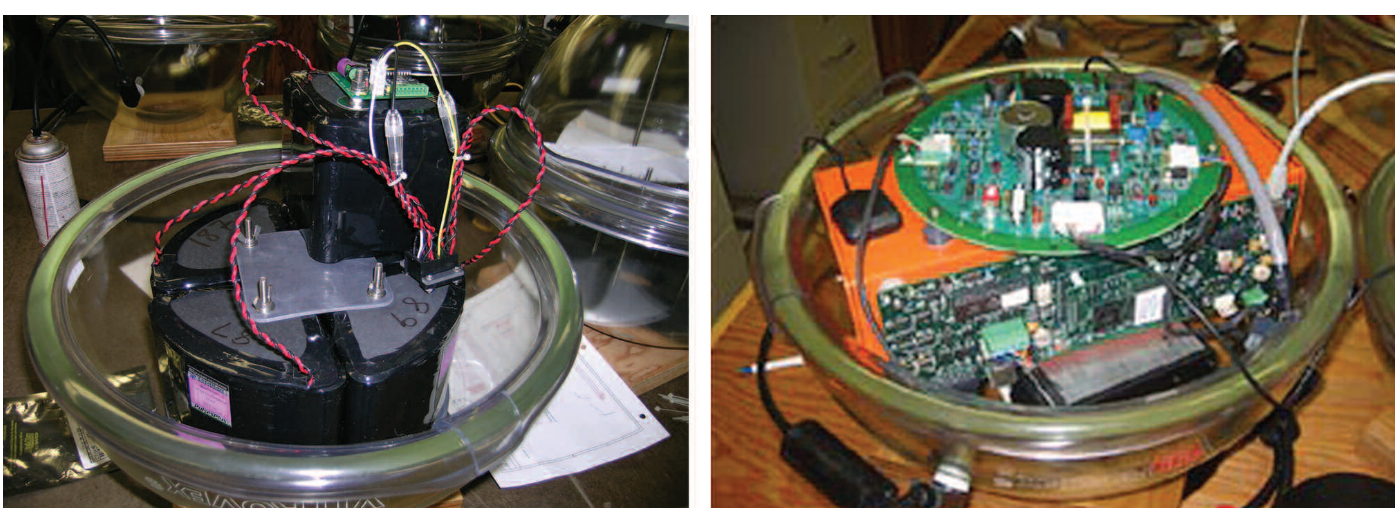


Photo 3 (a & b): Two opened glass spheres, one with primary lithium batteries (left) and one with electronics (right).

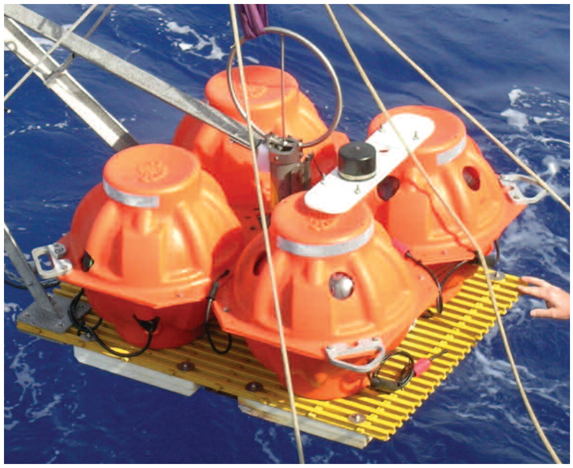


Photo 4: In this long deployment ocean bottom seismograph, four orange fiberglass "hardhats" are mounted on a plastic grillwork containing primary lithium batteries and electronics.

Based on an internal investigation, the direct cause of the fire and subsequent explosion was the unintended application of external voltage to a primary lithium battery pack housed in a sealed glass sphere that was not protected with an output diode. The investigation identified corrective actions, including both engineering and administrative controls, to help prevent recurrence of this incident. For comparison, Photo 5 presents the undamaged battery pack, where layers A-D represent the various lithium battery cell layers that make up the battery pack, and Photo 6 shows a damaged battery pack from the OBS after the fire and explosion.

Since 2000, tens of millions of Li-ion batteries have been recalled by various battery, computer and electronics manufacturers including Acer, Apple, Dell, Kyocera, Hewlett-Packard, Lenovo, Nokia and Sony (CPSC, 2009). These recalls were prompted by reports of batteries overheating and the potential for cell fires and explosions.

Compared to other rechargeable batteries (e.g., nickel metal hydride, nickel cadmium), Li-ion batteries are not as durable and can become hazardous if mishandled. They may explode if overheated or if charged to an excessively high voltage and require internal protection circuitry to help maintain safe operation (GPIL, 2009). In response to the hazards posed by primary and secondary lithium batteries, UL (2005) issued a lithium battery standard.

In December 2004 and again in August 2007, DOT (2004; 2007; 2009) tightened its safety standards for transport of primary and secondary lithium batteries. This regulatory action was in response to multiple fires involving lithium batteries, including a significant fire that occurred at Los Angeles International Airport (LAX) on April 28, 1999, which involved two pallets of primary lithium batteries. DOT reported that the packages were damaged during handling at LAX, the fire could not be extinguished with portable fire extinguishers and a fire hose, and that the incident illustrated the unique transportation safety problems posed by lithium batteries. These include risk of rough handling in transit, resulting short-circuiting and ignition of adjacent batteries.

DOT also considered the results of testing conducted by Federal Aviation Administration (FAA, 2004) to determine the behavior of primary lithium batteries when exposed to fire in a simulated aircraft cargo compartment. FAA's testing revealed that once ignited, lithium metal batteries can self-propagate the fire by igniting adjacent batteries until all batteries are engulfed in the fire. It was determined that the Halon fire extinguishing systems used in aircraft cargo compartments would not extinguish the primary lithium battery fire and that the pressure pulse from the burning batteries had the potential to breach the cargo compartment liner and spread the fire into the aircraft.

Rechargeable Li-ion batteries have also been evaluated by FAA (2006). These batteries also came under the scrutiny of DOT and FAA following the in-flight fire on a United Parcel Service DC-8 freighter aircraft that was on approach to land in Philadelphia in 2006 (NTSB, 2007). However, FAA concluded that Halon was able to extinguish the Li-ion battery fire in the test.

Regarding transportation safety, DOT concluded that lithium batteries, like other products which contain hazardous materials, can be transported safely provided appropriate precautions are taken in design, packaging, handling and emergency response. With respect to lithium battery risks, DOT (2007) states that 1) the risks that a lithium battery will short-circuit or rupture are a function of design, packaging and handling; and 2) the degree of risk posed is largely a function of the amount of stored energy.

Comprehensive Safety Program

In response to the various internal and external incidents involving primary and secondary lithium batteries, WHOI developed a comprehensive lithium battery safety program in 2006. The program is integrated into WHOI's overall safety management program, which includes routine safety inspections, accident/incident reporting and investigation, training and other key program elements. The intent of the safety inspection program is to proactively identify and correct hazardous conditions. The accident/incident program is designed to identify the causes of accidents and incidents, share lessons learned and prevent recurrence.

Key elements of the lithium battery safety program include documented safety guidelines and training. These guidelines address storage, handling, hazard analysis, battery pack design and fabrication, shipment, waste management and emergency situations. These guidelines are available on the institute's website, http://ehs.whoi.edu. Lithium battery safety training is provided for personnel who design, handle, fabricate, deploy and/or ship lithium and Li-ion battery packs and cells. Safety procedures during normal and emergency conditions are covered during this training.

Hazard Analysis

Battery pack designers and engineers are responsible for performing a hazard analysis (system safety analysis) to identify the various failure modes and hazards associated with the proposed configuration and type(s) and number of batteries used. Based on this analysis, safety-related design and testing criteria are incorporated into battery pack designs. As necessary, battery pack engineers and designers also develop standard operating procedures that include methods to identify and mitigate possible battery

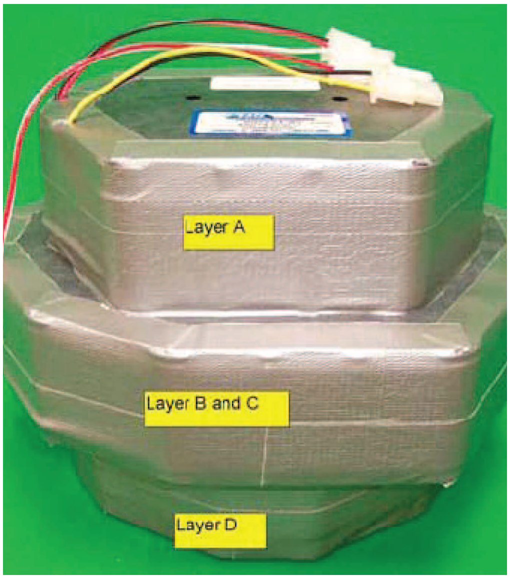


Photo 5 (left) shows an undamaged battery pack, where layers A-D represent the various lithium battery cell layers that make up the battery pack. Photo 6 (right) shows a damaged primary lithium battery pack after fire and explosion in OBS.

cell and pack failures that may occur during assembly, deployment, data acquisition/retrieval, transportation, storage and disassembly/disposal.

To increase the safety margin and decrease the failure rate, the hazard analysis process should be implemented during the design phase. This can be critical for battery pack designs, where a single cell failure could give rise to an increased hazard, involving a fire with multiple cells or the entire battery pack. Numerous hazard analysis methods may be used, from simple/preliminary to more complex (Vincoli, 2006). Examples include energy trace and barrier analysis, failure mode and effect analysis, fault hazard analysis, fault tree analysis, hazard and operability study, preliminary hazard analysis and what-if analysis. The method selected should be appropriate for the system design.

Safer Battery Packs

The design of a battery pack can adversely affect the safety characteristics of individual cells. For example, a series configuration may increase the potential for subjecting cells to forced over discharge conditions and parallel strings can lead to charging currents (ECP, 2006). Battery packs should be designed to avoid conditions that lead to short-circuiting, forced over discharging, charging or heating. This can be accomplished through proper design and use of protective devices such as fuses, thermal switches, heat sinks and diodes.

Based on the hazard analysis, feasible controls can be identified and incorporated into the battery pack design. The intent of incorporating feasible controls during the design phase is to increase the likelihood that the battery packs will perform reliably and safely during their entire life cycle. In general, it is more cost-effective to incorporate engineering controls during the design phase rather than after the battery packs have been fabricated.

Basic hazard controls and design recommendations that should be considered during the design phase include the following:

- Always use the same size cells in series or parallel connections. Do not mix cell chemistries and different cell sizes. Follow manufacturer's instructions and review MSDS for the battery cells being used.
- Primary lithium cells should not be connected to a power source or otherwise charged. When possible, use series diodes to block any possible charging current from entering through the discharge terminal.
- Cells fabricated into a battery pack should be of the same age (lot code) and history. Partially discharged or discharged cells should not be mixed in a pack or stored with new cells.
- Thermal cutoff or resetable polymeric, positive temperature coefficient resistors can be used to limit cell temperature rise when that rise is caused by external current flow through the protective device.
- Both the surrounding thermal environment and the heat output of a battery pack and/or individual cells should be evaluated. If the hazard analysis determines that a remote means of monitoring cell temperature may be needed, devices such as thermocouples and infrared temperature sensors should be considered. For larger packs or for batteries run at high output rates, additional thermal management must be considered. For example, copper or aluminum heat sinks could be incorporated into the pack design to effectively conduct excessive heat away from the cells during discharge.
- Cells connected in series should not contain connections to cells within the string, other than for cell voltage monitoring. This will reduce the possibility of cells being unequally discharged.
- Batteries should not be encapsulated without first consulting the manufacturer.
- Battery pack construction should take into account the need for cell vents. There should be an unrestricted escape path for the fumes such that pressure does not build up in the battery pack or housing. A vent mechanism should also be incorporated in rigid housings to avoid rupture or an explosion in the event of overpressure.
- Shock and vibration requirements must be considered as well. All cells must be protected from excessive shock and vibration.
- Regulations specific to the mode of transportation (air, land, water) to be used may limit the amount of lithium in any one container. Therefore, large packs may need to be designed in a modular fashion and assembled in the field. Verify potential shipping requirements and limitations prior to the final design.

Fabrication & Storage

After the battery pack design is complete, the next step is fabrication of the battery packs. During fabrica-

WHOI's Fire Extinguisher Criteria

Battery type: Lithium, primary nonrechargeable

Fire involves batteries only (cells or battery pack): Use Lith-X Class D extinguishing agent. DO NOT use water.

Fire involves batteries and other surrounding materials: Use an ABC dry chemical extinguisher or water hose stream. Fight the fire based on the fueling material (e.g., paper, plastic, solvent).

Battery type: Lithium-ion, secondary rechargeable

Fire involves batteries only (cells or battery pack): Use an ABC dry chemical extinguisher or water hose stream. Fight the fire based on the fueling material (e.g., paper, plastic, solvent).

Fire involves batteries and other surrounding materials: Use an ABC dry chemical extinguisher or water hose stream. Fight the fire based on the fueling material (e.g., paper, plastic, solvent).

tion, it is important to follow the design drawings and associated procedures. In accordance with quality control procedures, battery packs should be inspected at various stages of production and the proper design verified. During and after fabrication, battery cells and packs will need to be safely stored. Basic safety precautions that should be followed during battery pack fabrication and storage include the following:

•Store cells in original manufacturer's container until they are ready to be assembled into battery packs. Store primary lithium cells in a cool, dry, well-ventilated location. Significant quantities of lithium batteries may need to be isolated from flammable and combustible materials during fabrication and storage. This can be achieved with flammable-rated cabinets.

•Do not allow positive and negative leads to contact. Loose wires should not be stripped until it is time to install a connector, or the connector harnesses should be assembled before attaching them to the cell terminals. If no connector is used, wire ends should be insulated. When cutting wires, only cut one wire at a time.

•If available, use nonconductive tools and avoid placing battery cells and packs on electrically conductive surfaces.

•Do not solder directly to cell case. Only solder to the free end of solder tabs that are welded to the case.

•All battery packs should be appropriately labeled with key information such as type of battery, its voltage, temperature limit, manufacturer name and date.

Emergency Procedures

As noted, WHOI has experienced the following emergency scenarios with primary lithium batteries: hot cells, vented cells, fires and explosions. In accordance with manufacturer's instructions, emergency response procedures should be developed for each possible scenario. Emergency response personnel should be adequately trained in accordance with OSHA's (2002) standard for hazardous waste operations and emergency response.

The electrolyte contained within primary lithium cells can cause severe irritation to the respiratory tract, eyes and skin. Depending upon the cell chemistries (ECP, 2006), venting from primary lithium batteries could result in the release of hazardous substances such as thionyl chloride, sulfuryl chloride, bromine, chlorine, hydrochloric acid, sulfur dioxide, highly acid wastewater and hydrogen gas from the reaction with water. Depending upon the cell chemistries, other hazardous substances can be released as well.

If a hot or vented cell situation exists, all personnel should be evacuated from the area. The area should be secured until the hot or vented cell is stabilized and removed. Hot cells that have been cleared of any short-circuit and that have cooled to ambient temperature should be neutralized with sodium bicarbonate. Vented cells also should be neutralized with sodium bicarbonate. After being stabilized, hot and vented cells should be disposed of as hazardous waste.

Emergency equipment that may be needed for responding to hot and vented lithium cells include:

•infrared temperature probe;

•helmet with high-impact-resistant face shield;

•body, arm, hand, eye, respiratory protection;

•nonconductive extended pliers;

•Class D fire extinguisher;

•readily available emergency shower and eyewash;

•4 to 6 mil plastic bags with sealing mechanism;

•sodium bicarbonate (baking soda) and universal absorbing material (e.g., vermiculite).

Lithium will burn in a normal atmosphere and reacts explosively with water to form hydrogen. The presence of minute amounts of water may ignite the material and the hydrogen gas. Lithium fires can also throw off highly reactive molten lithium metal particles. Cells adjacent to any burning material could overheat and ignite.

In general, an extinguishing agent that is best suited to extinguish the bulk of the fuel that is involved in the fire should be used. For example, if a single primary lithium battery cell were to start burning, a Lith-X (Class D) extinguisher should be used to extinguish the fire. If other combustibles catch fire as result of the lithium battery, then use the appropriate extinguishing agent to extinguish these secondary fires.

Li-ion battery chemistry is not as safe as other rechargeable battery types, such as nickel metal hydride and nickel cadmium, and Li-ion batteries may explode if overheated or if charged to an excessively high voltage (GPIL, 2009). FAA (2006) conducted a series of tests to determine flammability of Li-ion batteries and concluded that flames produced by the batteries are hot enough to cause adjacent cells to vent and ignite.

While primary lithium battery fires cannot be suppressed with Halon, FAA concluded that Halon is effective in suppressing Li-ion fires. Because there is no metallic lithium in an Li-ion battery, ordinary extinguishing agents (e.g., ABC extinguisher) can generally be used for these fires. However, it is important to review the battery manufacturer's MSDS for the specific battery type to ensure that the appropriate fire extinguishing agents and procedures are available. The sidebar at left presents WHOI's generalized fire extinguisher selection criteria for lithium and Li-ion battery users.

Waste Management & Transportation

WHOI has established universal and hazardous waste management programs that include documented procedures, generator training, internal inspections, waste generation tracking, designated collection points, online waste pickup requests and waste minimization. It should be noted that there are significantly different regulatory requirements for management of universal and hazardous waste, including on-site accumulation times, labeling of collection containers, documentation (nonhazardous waste versus uniform hazardous waste manifest) and generator weight limits.

Primary lithium batteries that are damaged (e.g., vented or burned) must be managed as hazardous waste. Photo 7 shows a hot lithium battery cell that was effectively neutralized with sodium bicarbonate and subsequently disposed of as hazardous waste. Unlike primary lithium batteries, undamaged Li-ion batteries are not considered hazardous waste and need not be managed as universal waste. While spent or used Li-ion batteries may not be regulated as a hazardous waste, DOT regulations must be reviewed for applicable requirements.

Undamaged lithium batteries where the lithium can be recovered and recycled can be managed as universal waste (EPA, 2005). Most spent or used primary lithium batteries are safely managed as universal waste at WHOI. Universal waste collection sites (Photo 8) are located in most buildings on the institute's two campuses.

In addition to training provided to lithium battery users and waste generators, the lids on the collection containers are posted with the following:

•Universal waste. Only lithium batteries may be disposed in this container.

•Improper mixing of incompatible batteries (e.g., alkaline) could cause a release of toxic substances or fire.

•Battery cells and packs must be clearly labeled *Lithium Batteries.*

•All exposed terminals must be protected to prevent short circuiting.

•Never expose lithium batteries to water. Corroded or otherwise damaged batteries must be collected as hazardous waste.

•Properly secure container lid after adding waste batteries.

Waste pickup and emergency contact numbers are also noted.

Conclusion

Lithium and Li-ion batteries have become more popular and are widely used in a variety of applications, including consumer products, medical devices, research, military and other applications. The same properties that make these batteries more popular, such as higher capacity and higher energy density, have increased the potential hazards when their energy is released at a fast, uncontrolled rate.

Tens of millions of Li-ion batteries have been recalled by manufacturers because of batteries overheating and the potential for cell fires and explosions. In response to multiple fires involving air transport of lithium batteries, DOT tightened the safety standards for transport of lithium and Li-ion batteries.

Photo 7 (left) shows neutralized lithium battery cells being managed as hazardous waste. Photo 8 (above) illustrates a universal waste collection point.

WHOI has experienced multiple incidents involving primary lithium batteries. In response to those incidents and those reported throughout industry, WHOI developed a comprehensive lithium battery safety program. Since doing so, all lithium battery pack designers, fabricators and users have been trained and are implementing applicable elements of the program. The rate and severity of incidents involving lithium batteries has significantly decreased at WHOI. ■

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