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Current Status of Environmental, Health, and Safety Issues of Lithium Ion Electric Vehicle Batteries

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Preface

Lithium ion batteries are a mid- to long-term candidate technology for electric vehicle (EV) propulsion. Understanding environmental, health, and safety (EH&S) issues associated with lithium ion batteries is an important step toward their commercialization. This report examines the EH&S issues associated with the use of lithium ion batteries as the energy source in EVs.

The Analytic Studies Division (ASD) prepared this report for the Electric and Hybrid Propulsion Division of the Office of Transportation Technologies in the U.S. Department of Energy (DOE). The report is intended to help DOE determine the direction of its research, development, and demonstration program for lithium ion technology, and is part of DOE's program for working with industry to commercialize lithium ion batteries for EVs. Previous EH&S reports were prepared by ASD for sodium-sulfur, nickel metal-hydride, and lithium solid polymer electrolyte EV batteries. The assessment of EH&S issues for advanced EV batteries is ongoing; future studies will build on this and previous analyses.

We are indebted to many people who helped us obtain information for this report. We wish to thank the many members of the ad hoc DOE Electric Vehicle Battery Readiness Working Group who generously offered their expertise by contributing to the environmental and shipping chapters of this report. In addition, we thank Andy Altemos, who played a key role in the shipping regulations analysis. We thank Laurie Charlton of Toxco and Mark Small of Sony Electronics, for helping us understand some of the recycling and reclamation aspects of lithium ion batteries. We thank Jeffery Hannapel for his assistance in reviewing environmental regulations. We thank Ken Heitner and Bob Helton of DOE for their leadership and support in directing and sponsoring the EH&S program and these assessments. Finally, Ray Sutula and Al Landgrebe of DOE, Russell Moy of Ford Motor Company, and Gary Henriksen and Don Vissers of Argonne National Laboratory provided invaluable guidance on lithium ion battery research.

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Executive Summary

The lithium ion system considered in this report uses lithium intercalation compounds as both positive and negative electrodes and has an organic liquid electrolyte. Oxides of nickel, cobalt, and manganese are used in the positive electrode, and carbon is used in the negative electrode. This report presents health and safety issues, environmental issues, and shipping requirements for lithium ion electric vehicle (EV) batteries.

A lithium-based electrochemical system can, in theory, achieve higher energy density than systems using other elements. The lithium ion system is less reactive and more reliable than present lithium metal systems and has possible performance advantages over some lithium solid polymer electrolyte batteries. However, the possibility of electrolyte spills could be a disadvantage of a liquid electrolyte system compared to a solid electrolyte.

The lithium ion system is a developing technology, so there is some uncertainty regarding which materials will be used in an EV-sized battery. This report reviews the materials presented in the open literature within the context of health and safety issues, considering intrinsic material hazards, mitigation of material hazards, and safety testing. Some possible lithium ion battery materials are toxic, carcinogenic, or could undergo chemical reactions that produce hazardous heat or gases. Toxic materials include lithium compounds, nickel compounds, arsenic compounds, and dimethoxyethane. Carcinogenic materials include nickel compounds, arsenic compounds, and (possibly) cobalt compounds, copper, and polypropylene. Lithiated negative electrode materials could be reactive. However, because information about the exact compounds that will be used in future batteries is proprietary, ongoing research will determine which specific hazards will apply.

Normally operating cells do not expose the user to significant burns or material hazards. Designing cells and batteries to achieve adequate performance is likely to mitigate material hazards, because engineering design for reliability and durability will also enhance safety. Design attributes can mitigate material hazards by containing the battery materials and reducing the chance of a hazardous chemical reaction. Thermal management of the battery system, electrical protection, containment of battery materials, and venting of gases can reduce the hazards of a lithium ion system. Workplace practices can mitigate occupational hazards, if they exist. However, further safety testing should be conducted on EV-sized lithium ion batteries.

Environmental issues for lithium ion batteries are also presented. Environmental regulations must be considered in the development of any new battery technology. Lithium ion battery manufacturing processes may produce water emissions, air emissions, and solid waste subject to U.S. Environmental Protection Agency regulations under the Clean Water Act, Clean Air Act Amendments of 1990, and the Resource Conservation and Recovery Act (RCRA).

Source reduction (reducing or eliminating waste at the source) is more environmentally desirable than recycling and should be explored before resorting to recycling. However, source reduction is

or reclamation of lithium ion battery systems may be easier if RCRA Subtitle C regulations for hazardous waste do not apply. Hence, hexafluoroarsenate is not desirable: the arsenic would likely be considered a characteristically hazardous waste because of its toxicity.

As EVs become more common, the increase in metals, plastics, and lithium salts that may be recovered from batteries may improve the economics of recovery. Manufacturers are evaluating the profitability of recovering metals that may be used in the lithium ion system. Instead of landfilling plastics, recycling should be attempted. Further research will be needed to develop a commercial process for recycling plastics from lithium ion batteries.

In addition to environmental issues, shipping requirements for lithium ion EV batteries are considered. Certain batteries are excepted from hazardous material shipping requirements. The report reviews the conditions under which certain batteries would be excepted. Batteries not meeting these conditions are considered hazardous materials that must be shipped in accordance with the applicable regulations.

While regulations exist for transporting batteries and cells that contain lithium metal or alloy, they generally impose restrictive weight limits and packaging requirements. Therefore, they may not be appropriate for the transport of lithium ion EV batteries. Furthermore, if lithium ion batteries pose a significantly reduced level, or a different type of hazard in transport compared with batteries that contain lithium metal, the introduction of new lithium ion shipping requirements could reduce the regulatory burdens of transport. Research on shipping hazards, especially on the rate at which water and lithium react in the negative electrode, will be needed to support any proposed regulatory revision.

In the absence of specific shipping provisions for lithium ion batteries, the report considers alternative scenarios for shipping lithium ion EV batteries under present regulations. The main factors that determine shipping requirements are whether the battery is cycled or uncycled; if cycled, how electrochemically active it is; and whether it has free electrolyte. Which shipping scenarios will apply depends on materials selection and chemical reactivity of those materials within the battery. Thus, factors that affect the shipping requirements may be controlled, in part, by the manufacturer. For example, the state of charge of batteries may be selected to reduce shipping requirements, and manufacturers may be able to select electrolyte and negative electrode designs that will reduce the regulatory burden of shipping requirements.

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Introduction

A variety of lithium-based electrochemical cells, including lithium solid polymer electrolyte and lithium ion, is under investigation for use in rechargeable batteries for electric vehicles (EVs). A previous report characterized the environmental, health, and safety (EH&S) issues of lithium solid polymer electrolyte batteries in EV applications (Corbus and Hammel 1995). This report will focus on the EH&S issues posed by lithium ion batteries in EVs; subsequent reports may address additional EH&S issues of lithium-based systems.

The lithium ion electrochemical system considered in this report consists of lithium intercalation compounds as positive and negative electrodes, and an organic liquid electrolyte. In contrast to the lithium solid polymer electrolyte system analyzed in a previous report, this report will focus on lithium ion batteries with a liquid electrolyte. Although the lithium solid polymer electrolyte systems include some with negative electrodes made from lithium metal foil, the lithium ion system considered here includes only lithium-intercalating carbon as a negative electrode.

This report relies on information in the open literature and on personal communication, rather than on proprietary research and development information. The construction of lithium ion batteries large enough for EV propulsion was not reported in the open literature as of May 1995. Therefore, most of this report will identify issues that surround the use of lithium ion cells and the smaller batteries that have been made and reported on. If lithium ion EV batteries are produced, their materials may differ from those used in the lithium ion cells and batteries considered here. In addition, batteries are composed of many cells, so even though the EH&S issues of lithium ion cells apply to lithium ion batteries, such batteries for EVs may have other EH&S issues that warrant further study.

Companies in the U.S., Japan, and Europe are developing lithium ion batteries for EV and consumer electronics applications. Sony, the first company to bring a lithium ion cell to market, is the source of much of the information on safety issues available in the open literature. Other companies that produce lithium ion batteries include Sanyo, Matsushita, A&T Battery, and Japan Storage Battery. Duracell and Varta are developing a lithium ion EV battery under contract with the U.S. Advanced Battery Consortium. Many other development efforts are also under way.

The following chapters of this report provide a background on lithium ion cell materials ("Background"), and present the issues lithium ion cells and batteries may raise in health and safety ("Health and Safety Issues for Lithium Ion Batteries"), the environment ("Environmental Issues for Lithium Ion Batteries"), and transport ("Shipping Requirements for Lithium Ion Batteries").

Background

This chapter will provide background on lithium ion cell chemistry and performance criteria for cell materials selection. Lithium ion cell and battery performance itself will not be examined in this report, except in reference to safety. Mayer (1994) has assessed the performance of lithium ion cells under conditions simulating EV applications.

Cell Chemistry

The lithium ion system considered here consists of an inorganic lithium-intercalating compound as positive electrode, a lithium salt in an organic liquid as electrolyte, and a lithium-intercalating carbon negative electrode. Some lithium ion systems have negative electrodes made of other materials besides carbon, but these will not be considered in this report. Possible cell materials considered in this report appear in Table 1. The name *lithium ion* distinguishes this system from those with lithium metal negative electrodes. Although some lithium solid polymer electrolyte cells have lithium-intercalating carbon negative electrodes, only cells employing an organic liquid electrolyte, not a solid polymer electrolyte, will be considered here.

The general reaction in the lithium ion system is:

$6C + Li_xM_yO_z \Longleftrightarrow Li_xC_6 + Li_{1-x}M_yO_z$ (overall)

$6C + xLi^+ + xe^- \Longleftrightarrow Li_xC_6$ (negative electrode)

$Li_xM_yO_z \Longleftrightarrow Li_{1-x}M_yO_z + xLi^+ + xe^-$ (positive electrode)

where the reactions proceed from left to right during charging;

$x \leq 1$;
M = Ni (nickel), Co (cobalt), Mn (manganese), (or some combination thereof);
O = O (oxygen)

The advantage of a lithium-based electrochemical system is that higher energy density may be achieved compared to batteries using other elements. The lithium ion electrochemistry offers reduced reactivity and increased reliability compared to lithium metal-based systems with liquid electrolytes. Lithium ion cells also can have an advantage compared to solid polymer electrolyte cells because adequate conductivity is easier to achieve in liquid electrolytes than in solid electrolytes. However, liquid electrolyte spills could increase hazards of batteries with liquid electrolytes compared to the solid polymer system.

Table 1. Materials List and Hazards Index

Negative electrode 9

- carbon

Negative electrode dopants 11

- phosphorus (P)
- boron (B)

Positive electrode 11

- lithium manganese oxide ($Li_xMn_2O_4$)
- lithium nickel oxide (Li_xNiO_2)
- lithium cobalt oxide (Li_xCoO_2)

Electrolyte solvent 13

- propylene carbonate (PC)
- ethylene carbonate (EC)
- diethyl carbonate (DEC)
- dimethyl carbonate (DMC)
- dimethoxyethane (DME)

Electrolyte salt 14

- lithium hexafluoroarsenate ($LiAsF_6$)*
- lithium hexafluorophosphate ($LiPF_6$)
- lithium tetrafluoroborate ($LiBF_4$)
- lithium (bis) trifluoromethanesulfonimide (Li TFSI)
- lithium tris (trifluoromethanesulfonyl) methide (Li Methide)
- lithium trifluoromethanesulfonate (Li Triflate)

Current collectors 16

- aluminum
- copper

Separator 16

- polypropylene (Celgard)

Binder 16

- polyvinylidene fluoride
- cell can
- nickel plated steel

* Because of its toxicity and carcinogenicity, $LiAsF_6$ does not appear to be a likely salt for commercialization. It is included for reference only.

Cell Materials Selection

The lithium ion cell chemistry has certain advantages compared to cells that use lithium metal, and compared to lithium solid polymer electrolyte cells, as indicated above. This consideration of cell materials selection will highlight performance criteria, described below, for the components of lithium ion cells, focusing on materials listed in Table l. In addition to materials listed in Table 1, there are many alternative materials, especially for the electrolyte. Performance criteria are a key consideration no matter which materials are ultimately chosen for a lithium ion EV battery. The materials in Table 1 are considered because they have been used, or seem likely to be used, in commercialized lithium ion cells. Lithium hexafluoroarsenate is an exception; it is included for reference although its toxicity and carcinogenicity probably preclude commercial use.

Optimizing the materials selected for the negative electrode, positive electrode, electrolyte, and additives is being actively researched. For the electrodes, performance criteria include stability and speedy, reversible intercalation of lithium. A large difference in potential between negative electrode and positive electrode is desirable. However, the potential at which lithium intercalates into the negative electrode should be high enough compared to that of lithium metal to avoid lithium plating during charge. The potential of the positive electrode is also limited by electrolyte decomposition at high voltage. Current collectors are needed that resist corrosion over the operating voltage range. The electrolyte influences lithium intercalation in the electrodes and corrosion of current collectors. Additional considerations in electrolyte selection are stability and conductivity. Beyond the performance considerations addressed here, material costs, fabrication costs, and EH&S issues are important in optimizing a lithium ion battery. This report does not examine material and fabrication costs in detail.

Negative Electrode Materials

Using lithium-intercalating carbon negative electrodes may avoid the disadvantages of present lithium metal negative electrodes. Some intrinsic material hazards of lithium metal are described in the chapter "Health and Safety Issues for Lithium Ion Batteries." The behavior of lithium metal within a cell can pose hazards, as the surface of the lithium metal negative electrodes changes with cycling, sometimes forming dendrites that penetrate the separator. This connects positive and negative electrodes and causes short circuits (Takehara and Kanamura 1993:1173). In present lithium metal technologies, the negative electrodes generally must contain excess lithium metal, because of inefficient plating during cycling. Exothermic electrolyte reactions with newly exposed metal surfaces may also occur (Wilkinson et al. 1990:85). Lithium-intercalating carbon negative electrodes eliminate these disadvantages of lithium metal negative electrodes under normal circumstances.

Although lithium-intercalating carbon has some advantages over lithium metal for negative electrodes, substituting a carbon negative electrode for a lithium metal negative electrode reduces the theoretical specific capacity and voltage (Abraham 1993:1240). To minimize performance penalties, the carbon negative electrode's structure should allow easy intercalation and deintercalation of lithium ions and allow lithium intercalation to approach its theoretical limit (Tarascon and Guyomard 1993:1226).

Dahn et al. (1993:1179) have examined the impact of carbon structure on its lithium intercalating behavior. In general, the ordered, layered structure of graphite produces higher capacity cells than more disordered carbon structures because it accommodates more lithium ions (Tarascon and Guyomard 1993:1226). Further research is needed to address the undesirable properties of ordered carbon, such as capacity loss upon cycling in certain electrolytes (Levy and Cieslak 1993:2). In addition to research on carbon structures for negative electrodes, effects of introducing small amounts of other elements into carbon negative electrodes have been studied. Such doping, with elements such as phosphorus and boron, may improve negative electrode capacity and safety (Way and Dahn 1994). Sony Corporation has patented phosphorus-doped lithium-intercalating carbons and their use in negative electrodes (Azuma et al. 1991).

Thermal stability of the negative electrode and the electrolyte is an important consideration for the safety of the lithium ion cell. Lithium-intercalated carbon negative electrodes will react with organic liquid electrolytes, a reaction that accelerates at high temperature and depends on the electrolyte materials, the state of charge, and the surface area of the carbon. According to von Sacken et al. (1994:288), among PC-based electrolytes, thermal stability varies with co-solvent as follows: (most thermally stable) EC > DME > DEC > DMC (least thermally stable). Charged negative electrode materials are more reactive than uncharged, because they contain more chemical energy. In addition, the surface area of the carbon used in the negative electrode significantly affects reactivity at elevated temperatures; higher surface area carbons are much more likely to react with electrolytes than are lower surface area carbons. For example, in one electrolyte, higher surface area carbons (~20 m reacted violently starting below 125°C, and lower surface area carbons (~6 m^2/g) were found to have much better thermal stability up to 180°C (von Sacken et al. 1994:286).

Positive Electrode Materials

Oxides of nickel, cobalt, and manganese are possible positive electrode materials for lithium ion cells because they intercalate lithium at high voltage (Guyomard and Tarascon 1992:937). A high-voltage positive electrode is desirable to achieve high output voltage and energy density (Tarascon and Guyomard 1993:1222); however, oxidizing the electrolyte at high voltage is a concern (Dominey 1994:137). Other desired properties of positive electrode materials include high capacity, reversible intercalation of lithium at a reasonable rate, chemical stability in air and in the cell, compatibility with the electrolyte, and cyclability over the voltage range used (Ebner et al. 1994:238; Guyomard and Tarascon 1992:937). Nickel, cobalt, and manganese oxides are good candidates based on these criteria, but research to characterize the performance of these and other single and mixed metal oxides continues.

Electrolyte Materials

The electrolyte in a lithium ion cell consists of a lithium salt dissolved in one or more aprotic organic liquids. The electrolyte must meet numerous, sometimes conflicting criteria, so finding an optimal combination of solute and solvent for the electrolyte in the lithium ion system is difficult. Reviews of lithium battery electrolytes, such as Blomgren (1983) and Dominey (1994), provide a detailed discussion of alternate electrolyte materials and their properties. Dominey (1994:137) indicates that important properties for an electrolyte for lithium ion batteries are high-voltage stability, low occurrence of co-intercalation at the negative electrode, and stability to reduction at the negative electrode.

Dominey and Blomgren both review characteristics of solvents and salts that are important for lithium batteries. In selecting a solvent for the electrolyte of a commercial lithium ion battery, Dominey considers "safety, long-term stability, and rate capability" to be the most important factors (Dominey 1994:139). Solvent characteristics that influence safety include "flash point, solvent volatility, toxicity," and response to thermal abuse (Dominey 1994:140). Long-term stability requires that the solvent be thermodynamically or kinetically stable with respect to other cell materials (Blomgren 1983:21). Good rate capability requires a highly conductive electrolyte (Dominey 1994:139).

Kinetic stability may be achieved by forming a stable interfacial film on one or both electrodes (Fong et al. 1990:2009, 2012). The film consists of products of the reaction between the electrolyte and the lithium in the negative electrode, and it forms during the first charging cycle. If this film is stable, it prevents further reactions between the electrolyte and the negative electrode during subsequent cycles.

Important characteristics that Dominey (1994:147) considers in the choice of salts for a lithium battery electrolyte are price, performance, and safety. Contributing to performance are conductivity, thermal stability, stability to oxidation and reduction, solubility, cycling efficiency, and performance at low and high temperatures.

Research has been conducted on a wide variety of lithium salts. Commonly used experimental salts include $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiClO_4$, and organic lithium salts, such as Li TFSI ($LiN(SO_2CF_3)_2$), Li Methide ($LiC(SO_2CF_3)_3$), and Li Triflate ($LiCF_3SO_3$) (Dominey 1994:148-149). With multiple factors to optimize, no salt is clearly preferred for all solvents, positive electrodes, and negative electrodes; however, $LiPF_6$ has been used in commercialized cells and has desirable properties including good oxidative and reductive stability, good conductivity, and relative safety. Stability to heat and moisture are important considerations for salt selection; the thermal and moisture instability of $LiPF_6$ can pose problems for lithium ion batteries. $LiBF_4$ has also been proposed for commercial use. $LiAsF_6$ has greater stability to heat and moisture than $LiPF_6$, and electrolytes using $LiAsF_6$ achieved the highest cycling efficiency in laboratory experiments (Dominey 1994:148). However, $LiAsF_6$ has not been proposed for use in commercial lithium ion EV batteries because its toxicity is a serious concern in a commercial system. Explosion hazards posed by $LiClO_4$ probably preclude its use in commercial systems (Dominey 1994:148).

The organic salts are the target of ongoing research and development efforts. Li Methide may offer slightly better conductivity than Li TFSI, under some conditions, but is much more expensive. Ongoing investigations focus on improving the conductivity of Li Triflate in polymer electrolytes, but it is unlikely to surpass the conductivity of Li TFSI, especially in liquid electrolytes (Armand and

Sanchez 1995). For all inorganic and organic salts, acute and chronic health effects will be considerations in the commercialization process.

The cyclic carbonates are frequently combined with another organic liquid in the electrolyte of lithium ion cells. Ethylene carbonate enhances the cycle life of lithium ion cells by forming a relatively stable interfacial film on the carbon negative electrode. It must be mixed with other solvents because pure EC has too high a melting point (Dominey 1994:144). One such combination that has good oxidative stability is a mixture of EC and an acyclic carbonate, DMC (Guyomard and Tarascon 1993:3071). Besides the carbonates, other organic liquids have been used experimentally in the electrolyte of lithium ion cells (Dominey 1994:139-147; Blomgren 1983:13-41).

Additives

Additives to the electrolyte may control unwanted reactions, such as electrolyte decomposition, and improve characteristics of interfacial films. Additives will not be considered further, because many possible additives exist and it is not clear which, if any, will be used.

Health and Safety Issues for Lithium Ion Batteries

This chapter examines health and safety hazards intrinsic to some possible materials for lithium ion cells and batteries, outlines measures to mitigate these hazards, and presents the safety status of lithium ion cells. Exact chemistries of future batteries are not known, so possible materials were selected based on the open literature and on existing lithium ion cells and battery systems.

Possible lithium ion cell and battery materials are shown in Table 1. Health and safety issues for some of these materials have been summarized by Archuleta (1994). The first section of this chapter, Intrinsic Material Hazards, examines the health and safety hazards lithium ion cell and battery materials may cause. Health and safety hazards of lithium and lithium compounds will be reviewed first, followed by consideration of negative electrode, positive electrode, electrolyte, and other material hazards. The second section, Mitigation of Intrinsic Material Hazards, examines design and workplace health and safety measures that can alleviate the material hazards. The third section, Safety Status, presents U.S. Army and Sony research on lithium ion cell safety.

Intrinsic Material Hazards

This section will present hazards intrinsic to materials that may be used in lithium ion EV batteries. Although possible hazards exist for some materials, design features and workplace practices can mitigate these hazards, as examined in the next section.

Three types of standards for occupational exposure are presented here. When material hazards occur in the workplace, the Occupational Safety and Health Administration (OSHA) may regulate the allowable worker exposure. Permissible Exposure Limits (PELs) establish time-weighted average amounts of airborne exposure permitted during any 8-hour shift of a 40-hour work week. The PEL is indicated below and in Table 2 if an exposure limit has been established for the material. The OSHA PELs listed in the table will become enforceable regulation once they are promulgated. The American Conference of Governmental and Industrial Hygienists (ACGIH) establishes Threshold Limit Values (TLVs) and Biological Exposure Indices (BEIs) to guide industrial hygiene practices. Threshold Limit Values and BEIs, like PELs, apply to 8-hour shifts of a 40-hour work week, but do not have the force of regulation. Threshold Limit Values establish time-weighted average amounts of airborne exposure, while BEIs indicate the level of a chemical in biological specimens.

Lithium and Lithium Compounds

This part of the Intrinsic Material Hazards section will describe the hazards of lithium compounds and lithium metal, in the workplace and in vehicles. Lithium compounds are used in both electrodes and in the electrolyte of lithium ion cells. Hazards of these compounds that arise from other elements will be considered in the parts below. This part presents hazards of lithium metal, even though, during normal operation, lithium ion cells do not contain lithium metal. Hazards of lithium metal may be relevant because lithium-intercalated carbon approaches the electrochemical potential of lithium metal, and may approach its reactivity. Further research is needed to determine the reactivity of lithium-intercalated carbon compounds. Until this research is complete, hazards of lithium metal reactions may be useful for reference.

Lithium compounds generally contain lithium as the ion, which is less reactive than lithium metal and presents fewer safety hazards. However, ionic lithium has acute toxicity effects and chronic effects on the central nervous system (Lewis 1992: 2127). Material Safety Data Sheets list effects of ionic lithium among the hazards of the lithium compounds of interest.

Lithium metal is a health and safety hazard because of its reactivity (Lewis 1992:2123). Lithium metal reacts with water to form hydrogen, a flammable gas. Metallic lithium reacts with moist air, and with a wide variety of other substances. Reactions with metallic lithium release heat and, in some cases, hazardous reaction products. Direct contact with lithium metal could cause severe chemical burns. Lithium metal is unlikely to be present during the manufacturing of lithium ion cells. Lithium compounds in the positive electrode and electrolyte salt will probably be used to introduce lithium into the cell, rather than lithium metal.

Exposure to ionic lithium could occur during manufacturing of lithium ion cells, either from the positive electrode material or from the electrolyte salt. After the cells were assembled, exposure to ionic lithium could occur only if cell containment failed. Likewise, in the unlikely event that lithium metal formed during cell cycling, people could be exposed to the metallic form if the cell container failed or during recycling. None of the PELs and TLVs applicable to the lithium compounds in lithium ion batteries were established because of effects of ionic lithium. Lithium hexafluoroarsenate is subject to a PEL and a TLV because of its arsenic content; $LiBF_4$ and $LiPF_6$ have a PEL and BEI as fluorides (see Table 2). Lithium nickel oxides and lithium manganese oxide have PELs and TLVs as compounds of nickel and manganese; lithium cobalt oxide has a TLV as a cobalt compound.

Negative Electrode Materials

Negative electrodes made from lithium-intercalating carbon are used in the lithium ion cell. Even when fully lithiated, they are less reactive than lithium metal, but further study of their reactivity is needed. Toxicologically they could present the hazards of lithium ion addressed in the preceding part, but further characterization is needed. These negative electrodes have been developed in response to several problems of present lithium metal negative electrodes, described in the "Background" chapter. They may have safety advantages over lithium, but there are hazards associated with lithium-intercalating carbon negative electrode materials, and with the reactions that may occur between these electrodes and the electrolyte.

Negative electrodes for lithium ion cells consist primarily of carbon. Graphite, a form of carbon that could be used in lithium ion cells, has PELs and TLVs (see Table 2). Carbon dust can irritate the eyes and mucous membranes (Lewis 1992:697). The amount of carbon dust generated in the workplace depends on the specific manufacturing process involved. In experimental studies on animals, carbon has affected the reproductive system (Lewis 1992:697).

Table 2. Occupational Standards for Lithium Ion Battery Materials

Species	Standard	Source
Aluminum (metal dust)	10 mg/m^3	1
Aluminum (pyro powders and welding fumes; as Al)	5 mg/m^3	1
Aluminum (metal, respirable fraction; as Al)	5 mg/m^3	2
Aluminum (metal, total dust; as Al)	15 mg/m^3	2
Arsenic (as As) (1: elemental and inorganic compounds) (2: inorganic compounds)	0.01 mg/m^3	1,2
Cobalt (elemental and inorganic compounds; as Co)	0.02 mg/m^3	1
Cobalt (metal, dust, and fume; as Co)	0.1 mg/m^3	2
Copper (fume)	0.2 mg/m^3	1
Copper (fume)	0.1 mg/m^3	2
Copper (dusts and mists; as Cu)	1 mg/m^3	1,2
Fluorides (as F)	2.5 mg/m^3	1,2
Graphite (all forms except graphite fibers; respirable fraction)	2 mg/m^3	1
Graphite, synthetic (respirable fraction)	5 mg/m^3	2
Graphite, synthetic (total dust)	15 mg/m^3	2
Graphite, natural (respirable dust)	15 x 10^6 particles/ft^3	2
Manganese (fume)	1 mg/m^{3*}	1
Manganese (as Mn) (1: dust and compounds) (2: compounds and fume)	5 mg/m^{3*}	1,2
Nickel (metal and insoluble compounds; as Ni)	1 mg/m^{3**}	1,2
Notice of Intent to Change Standard to: * 0.2 mg/m^3 ** 0.05 mg/m^3 (ACGIH)	Sources: 1. ACGIH 1994-1995 2. 29 Code of Federal Regulations 1910 (OSHA)	

Phosphorus and boron compounds have been proposed as negative electrode additives. Phosphorus compounds are in use in commercial cells. It is uncertain whether boron compounds will be used. Intrinsic material hazards of negative electrode additives will need additional investigation. Health and safety issues during manufacture would likely be a concern because toxic and hazardous substances such as boron trichloride may be used to supply the boron (Way and Dahn 1994:908); phosphoric acid (has a PEL and a TLV), phosphorus pentoxide, or phosphorus trioxide may be used to supply the phosphorus. If phosphorus or boron were added to the negative electrode, the intrinsic material hazards of the specific fabrication process would need to be evaluated.

In addition to the intrinsic material hazards of the negative electrode, exposing lithium ion cells to elevated temperatures causes exothermic reactions between the negative electrode and the electrolyte, and may release dangerous quantities of heat and gaseous reaction products such as ethylene, propylene, and carbon dioxide. Lithium metal negative electrodes react with electrolytes more readily than do lithium-intercalated carbon electrodes, but the latter will still undergo reactions. Experiments indicated that the thermal stability of lithium-intercalated carbon in electrolyte varied depending on the electrolyte, state of charge, and electrode surface area, as detailed in the "Background" chapter (von Sacken et al. 1994).

Considering occupational and in-vehicle exposure to these hazards, exposure to carbon, phosphorus compounds, or boron compounds could occur during manufacturing of negative electrode materials, or during recycling. Dust would be the main source of exposure to carbon. Because fabricated electrodes contain binders, dust exposure would be much less of a concern during recycling than during manufacturing. Permissible Exposure Limits and TLVs for graphite and phosphoric acid are indicated in Table 2. Carbon, phosphorus, or boron exposure is unlikely while the cells are intact. In-vehicle exposure to negative electrode materials could occur only under extreme conditions of battery destruction. In-vehicle or occupational exposure to the heat and reaction products generated in the electrolyte-electrode reaction would occur only under the abnormal conditions of elevated battery temperature that cause this reaction.

Positive Electrode Materials

This part of the Intrinsic Material Hazards section considers the hazards of positive electrode materials, including the significance for workplace and in-vehicle safety. The positive electrodes in lithium ion cells are made of inorganic lithium intercalation compounds. As lithium compounds, these materials present the hazards of ionic lithium, considered above. In addition, these materials may pose hazards as compounds of the other metals they contain.

Positive electrode compositions of particular interest in recent research and development efforts are the nickel, cobalt, and manganese oxides, $LiNiO_2$, $LiCoO_2$, and $LiMn_2O_4$. In addition to pure $LiNiO_2$, $LiCoO_2$, and $LiMn_2O_4$, mixed metal oxides such as $LiNi_yCo_{1-y}O_2$, are being investigated. The hazards of the oxides of pure nickel, cobalt, or manganese, and their decomposition at high temperature are reviewed below. Mixed metal oxides could present hazards of the compounds of all metals they contain. Their thermal decomposition behavior could differ from the pure metal oxides. Because of the wide variety of combinations possible, characteristics of mixed metal oxides will not be examined further.

Regarding the reactivity of the oxides of manganese, nickel, and cobalt, $Li_xMn_2O_4$, Li_xNiO_2, and Li_xCoO_2 are all air and moisture stable (Tarascon and Guyomard 1993:1222). All three have hazardous decomposition products. Lithium manganese oxide (Johnson Matthey 1995a) and lithium nickel oxide (Advanced Materials) can react to produce strong bases. Lithium cobalt oxide can decompose to hazardous cobalt oxides (Johnson Matthey 1994).

Manganese compounds, including $Li_xMn_2O_4$, are subject to a PEL and have a TLV (see Table 2). These standards were established in response to human health effects of manganese compounds such as chronic manganese poisoning, which can damage the central nervous system and lungs. Changes in the blood and lungs of experimental animals also contributed to the establishment of standards for manganese (ACGIH 1991). Chronic manganese poisoning usually occurs after manganese dusts are inhaled over several years, but may occur after 3 months of heavy exposure (Johnson Matthey 1995a; Lewis 1992:2161). Poisoning from ingestion is uncommon (Lewis 1992:2161), but may cause lethargy and edema (Johnson Matthey 1995a).

Insoluble nickel compounds, such as Li_xNiO_2, have a PEL and a TLV (see Table 2). The ACGIH has issued a notice of intent to change the TLV for insoluble nickel compounds, and to reclassify them as confirmed human carcinogens (ACGIH 1994). In addition to carcinogenicity, this TLV was established because nickel compounds damage the lungs of experimental animals. Skin sensitivity among workers exposed to nickel is also a concern, but the TLV may not provide protection from this health effect. The National Institutes for Occupational Safety and Health have recommended that the PEL for nickel compounds be reduced to 0.015 mg/m^3, based on evidence of carcinogenicity (ACGIH 1991).

Inorganic cobalt compounds, including Li_xCoO_2, have TLVs, but only cobalt metal dust and fumes have PELs. ACGIH also classifies inorganic cobalt compounds as animal carcinogens (ACGIH 1994). Acute exposure to cobalt compounds may irritate the digestive system (if ingested), respiratory system (if inhaled), skin, and eyes. Cobalt compounds may aggravate existing respiratory disease. Acute exposure may also repress the production of erythrocytes (Johnson Matthey 1994).

Besides these material hazards, exposing positive electrode materials to elevated temperatures causes chemical reactions that release oxygen gas. Positive electrode materials in their charged state are less stable at high temperatures than in their uncharged state. Of the three positive electrode materials considered here, oxygen is released for Li_xNiO_2 at the lowest temperature (between 150° and 200°C), Li_xCoO_2 at an intermediate range (starting at 220°C), and $Li_xMn_2O_4$ at the highest temperature (higher than 300°C). Oxygen could present a safety hazard by raising the pressure inside the cell (Dahn et al. 1994).

In-vehicle and workplace exposure to positive electrode materials is possible during lithium ion positive electrode material manufacturing, during cell assembly, or during processing of spent batteries. Compounds of nickel, cobalt, and manganese have PELs and TLVs, as indicated in Table 2. Exposure is unlikely while cells are intact. In-vehicle exposure to these materials could occur only during the destruction of the battery. The decomposition of positive electrode materials to release oxygen could occur only if the battery were heated far beyond its normal operating temperature.

Electrolyte Materials

The hazards of the electrolyte are considered in this part of the Intrinsic Material Hazards section. The electrolyte in a lithium ion cell consists of a lithium salt dissolved in one or more organic liquids. Using a liquid electrolyte instead of a solid electrolyte raises the possibility of electrolyte spills. The cyclic carbonates, especially EC, are likely choices for the predominant organic liquid. They may be combined with some other organic liquid, such as DEC, DMC, or DME. Lithium salts that are likely candidates include inorganic and organic salts. This part presents the hazards of these electrolyte materials and their decomposition reactions. The "Background" chapter provides background information on alternative electrolyte salts and solvents, and desired electrolyte properties.

The organic liquids that may form the bulk of the electrolyte (PC and EC) are both mildly toxic when ingested and irritate eyes and skin. They are flammable liquids (Lewis 1992:699, 1799). They are stable, but will react with oxidizing agents, acids, and bases, especially when heated (Huls Canada Inc. 1992a; 1992b) Their thermal decomposition produces irritating fumes (Lewis 1992:699, 1799). Propylene carbonate may also react with water, and will slowly oxidize in air (J.T. Baker Inc. 1994a). Ethylene carbonate should not be exposed to reducing agents (Huls Canada Inc. 1992b).

The other organic liquids that may be used (DEC, DMC, and DME) vary somewhat in their health effects. Inhaling DEC may cause nausea, vomiting, or headache. Skin and eye contact may cause irritation. Diethyl carbonate is highly flammable. When heated, its decomposition products include acrid smoke and fumes (Lewis 1992:1214). It will react with strong oxidizing agents (J.T. Baker, Inc. 1994b).

Inhaling DMC may cause weakness, nausea, or respiratory problems. It irritates the eyes and skin (PPG Industries, Inc. 1994). Acute effects include kidney disorders. It is a highly flammable liquid, and reacts with oxidizing and reducing agents, strong acids and bases, and moist air or water (Sigma-Aldrich). It decomposes when heated, releasing carbon dioxide and methyl alcohol (PPG Industries, Inc. 1994).

Dimethoxyethane is hazardous to fetal development. Its chronic effects include liver, kidney, blood, central nervous system, and reproductive disorders. Acute effects caused by inhaling, ingesting, or skin contact include irritation. It is very flammable, and may react with oxidizing agents and strong acids (Sigma-Aldrich 1992). Light, heat, and air may cause hazardous reactions (Lewis 1992:1317).

The organic liquids that may be used in lithium ion batteries are volatile. In poorly ventilated conditions, vapors from these liquids may reach dangerous concentrations, such that the gas displaces too much air. If an exposed individual receives insufficient oxygen, unconsciousness or death may result. Similarly, decomposing or burning any electrolyte organic liquid may produce asphyxiants (carbon dioxide and carbon monoxide).

The possible lithium salts for the electrolyte present the health hazards of lithium ion, addressed in the part on lithium and its compounds. Lithium tetrafluoroborate, $LiAsF_6$, and $LiPF_6$ are all inorganic fluorides, a group of compounds which have a PEL and a TLV because they are toxic and irritating. Chronic exposure to fluorides can cause bone damage, hypertension, and kidney damage (ACGIH 1991). Material Safety Data Sheet descriptions of effects of these salts include irritation or burns of the skin and eyes, irritation of the lungs, bone and teeth problems, weight loss, anorexia, and anemia (Johnson Matthey 1989; 1995b). These compounds are air and moisture stable, but decompose to hazardous products, including toxic, corrosive fumes of hydrogen fluoride (Johnson Matthey 1989; 1991; 1995b; Strem Chemicals, Inc. 1991; 1992).

Lithium hexafluoroarsenate has a PEL and a TLV as an arsenic compound. ACGIH (1994) classifies arsenic compounds as confirmed human carcinogens. Overexposure affects the digestive, circulatory, respiratory, and nervous systems, skin, and bones (Strem Chemicals, Inc. 1991). Skin contact and ingestion are the most dangerous paths of entry into the body during acute exposure (Strem Chemicals, Inc. 1991), but inhalation can also be fatal (Sigma-Aldrich 1995a). Lithium hexafluoroarsenate will react with active metals (Strem Chemicals, Inc. 1991). Hazardous combustion or decomposition products include hydrogen fluoride and arsenic oxides (Sigma-Aldrich 1995a).

Although $LiPF_6$ is less toxic than $LiAsF_6$, overexposure affects the digestive, circulatory, respiratory, and nervous systems, skin, and bones (Strem Chemicals, Inc. 1992). Ingestion is the most dangerous path of entry into the body, but inhalation and skin contact can also be harmful (Sigma-Aldrich 1995b). Lithium hexafluorophosphate will react with mineral acids, oxidizing agents, and active metals (Strem Chemicals, Inc. 1992). It will react with water, yielding hydrofluoric acid. Hazardous combustion or decomposition products include hydrogen fluoride, phosphorus oxides, and phosphine (not to be confused with phosgene) (Sigma-Aldrich 1995b).

Lithium tetrafluoroborate can cause the health problems associated with ionic lithium and fluorides, indicated previously. It can react with strong acids to produce hydrogen fluoride, and decomposes when heated to produce boron trifluoride (Johnson Matthey 1989), which has a PEL and an ACGIH Short-Term Exposure Limit (ACGIH 1994).

Lithium TFSI is found to be moderately toxic by ingestion and slightly toxic by skin exposure, based on experiments on animals. It was extremely irritating and corrosive to the eyes and skin. In a salmonella/mammalian-microsome reverse mutation assay, Li TFSI did not produce mutations. It can decompose to carbon monoxide, carbon dioxide, nitrogen oxides, sulfur oxides, and hydrogen fluoride (3M 1992; 1995a).

Lithium Methide inhalation, ingestion, and skin and eye exposure should be avoided. Lithium Methide may release toxic substances, including hydrogen fluoride, upon thermal decomposition. However, thermal decomposition is unlikely below 275°C (Covalent Associates, Inc.).

Lithium Triflate can cause moderate eye irritation and mild skin irritation. Upper respiratory irritation may occur because of inhalation overexposure. Ingestion may cause illness. Lithium Triflate may be absorbed during skin contact or inhalation, and may remain in the body for some time. Decomposition products of Lithium Triflate include carbon monoxide, carbon dioxide, nitrogen oxides, sulfur oxides, and hydrogen fluoride (3M 1995b).

Besides these hazards of electrolyte materials, electrolyte decomposition can be hazardous. Overheating accelerates the electrochemical reactions that cause electrolyte decomposition. Some electrolyte reduction always occurs during the initial formation of the interfacial film at the surface of the carbon negative electrode, during the first charging cycle (Fong et al. 1990) (see "Background"). With certain combinations of negative electrode and electrolyte materials, additional electrolyte decomposition at the negative electrode occurs during subsequent cycles (Peled et al. 1993). Commonly used organic solvents EC and PC evolve flammable gases (ethylene and propylene, respectively) during reduction reactions. Electrolytes may also decompose when the voltage at the positive electrode is high enough to oxidize the organic solvent. As examined in "Background," lithium ion cells are designed with high-voltage positive electrodes. Tarascon and Guyomard (1993:1222) have researched electrolytes that are stable to high voltages.

In addition to electrolyte decomposition, electrolyte phase changes can pose hazards. The organic liquids identified for possible use in lithium ion electrolytes have boiling points in the range of 60° to 250°C under standard conditions. The boiling point of any proposed electrolyte is a key factor, as vaporizing the electrolyte would damage the integrity of the cell.

Exposure to electrolyte materials can occur during the manufacturing process. None of the organic solvents presented above as possible electrolyte materials have PELs. The inorganic salts ($LiPF_6$, $LiBF_4$, and $LiAsF_6$) are fluorides, a group of compounds that has a PEL, as indicated in Table 2. After cell manufacturing is complete, exposure to electrolyte materials is possible if cell and battery containers are breached. For example, vehicle passengers could be exposed if containment failed and the electrolyte leaked. Electrolytes may be more likely to leak when a new cell is damaged than when a cycled cell is damaged: new cells contain more electrolyte than cycled cells, because some electrolyte is consumed during cycling. Exposure could also occur during processing of used batteries. Overheating, overcharging, and overdischarging can cause decomposition or phase changes in the electrolyte, posing hazards of exposure to electrolyte decomposition products or gaseous electrolyte compounds.

Other Cell Materials

Table 3 summarizes hazards of other possible lithium ion cell materials. The existing PELs for these materials appear in Table 2.

Exposure to these other cell materials could occur during manufacturing. Once cells are complete, exposure to aluminum, copper, and nickel would be unlikely. Battery overheating and venting could cause exposure to the fumes from the decomposition of polypropylene and polyvinylidene fluoride.

Table 3. Material Hazards Summary

Material	Hazard	Examples of Reactions to Avoid
Aluminum (as powder)	reactive metal lung damage when inhaled	metal oxides, silver chloride, ammonium nitrate, and sulfides.
Copper	questionable carcinogen nausea, vomiting upon ingestion	chlorine, fluorine, sulfuric acid, and potassium dioxide
Polypropylene	questionable carcinogen (probably due to residual reactants) decomposes to irritating fumes when heated	
Polyvinylidene Fluoride	very mild toxin when inhaled decomposes to highly toxic fumes when heated	
Nickel Plated Steel	nickel: same PEL and TLV as insoluble compounds of nickel (see text)	(powder) air, oxidants

(Lewis 1992)

Mitigation of Intrinsic Material Hazards

The intrinsic material hazards of some of the possible lithium ion battery materials can be mitigated through battery design and workplace procedures, as shown in this section.

Safety in Battery Design

This part considers how cell, battery, and vehicle design could mitigate some intrinsic material hazards. Thermal management system, electrical system, containment, and venting design issues for lithium ion EV batteries are addressed.

Using integrated circuits to monitor cells may assist thermal and electrical management. In the small lithium ion batteries that have been commercialized, individual cells are usually monitored for voltage, temperature, and current. However, monitoring and control of EV-sized batteries may differ substantially from small batteries in consumer electronics applications.

Thermal Management System

As indicated in the discussion of intrinsic material hazards, exposing lithium ion cells and batteries to elevated temperatures could cause hazardous conditions such as exothermic and gas-producing reactions. In an EV, heat from the battery itself, or from other components, could raise battery temperature to unsafe levels if no thermal management system were present. The thermal management system for a lithium ion EV battery could mitigate these hazards by keeping battery temperature below a maximum design temperature, where the exact maximum design temperature would be established to protect the materials in the battery. The actual design temperature of the thermal management system, which would be selected for battery performance, would probably be lower than the maximum design temperature. For example, for performance reasons, recommended charging temperatures for Sony LIP-802 lithium ion batteries are 0° to 40°C and for Yardney YLI-P5 batteries, 0° to 45°C. Recommended discharging temperatures are -20° to 60°C for both batteries (Igarashi et al. 1995:347; Reddy et al. 1995:312). A thermal management system designed to maintain this temperature range during normal battery use would mitigate the hazards of exposing battery materials to high temperatures.

In addition to thermal management during normal battery use, designing fail-safe measures to mitigate thermal hazards during failure modes can improve safety. For example, research and development is under way to prevent thermal runaway with heat sensitive (shut-down) separators that stop electrochemical reactions (Spotnitz et al. 1995:127).

Electrical System

Electrical abuse of the lithium ion cells could pose material hazards. For example, short circuits could raise the cell temperature, making reactions between the negative electrode and the electrolyte more likely; excursion from the range of potential in which the electrolyte is stable could cause its decomposition. However, designing lithium ion cells for performance is likely to mitigate such material hazards, because electrical abuse must be prevented to ensure cell durability. Selecting abuse-tolerant materials and protecting cells within the battery against overcharge and overdischarge will simultaneously promote cell performance and safety.

Overcharge and overdischarge protection may be achieved through two complementary approaches: adjusting the cell chemistry to minimize the effects of overcharge and overdischarge, and providing protective electrical circuits. Cell chemistry may be adjusted to protect the electrolyte from oxidation during overcharge by introducing an electrolyte additive that will reversibly oxidize above the normal maximum positive electrode potential, and below the potential at which the bulk electrolyte material oxidizes (Dominey 1994:156). Overcharge and overdischarge protection may be enhanced by ensuring that each cell contains a chemically balanced amount of positive and negative electrode materials (Ebner et al. 1994:245).

Electrical circuits may also provide cell protection against overcharge and overdischarge by using external fuses or internal safety mechanisms, as in Sony's cells. The internal electrical safety mechanism in the Sony cell operates during accidental overcharge, when gas evolves, raising internal pressure until a vent opens, breaking the circuit (Ozawa and Yokokawa 1993:1).

Containment

The lithium ion system described in this report uses an organic liquid electrolyte, which may cause hazardous electrolyte spills if cells are damaged. The design of the cell and battery container and seals can help prevent electrolyte spills. Minimizing the amount of electrolyte in the cell can limit the severity of spills that occur in spite of containment and seals. For example, some of Sony's lithium ion cells contain little excess electrolyte, as demonstrated in safety tests described in the Safety Status section. Enough electrolyte to conduct ions throughout the life of the cell must be used, allowing for electrolyte decomposition during cycling.

Venting

Although normal cell reactions do not generate excessive amounts of gas, pressure buildup caused by gas formation results from several undesirable reactions during failure modes. Gaseous decomposition products of cell materials are identified in the Intrinsic Material Hazards section. To avoid explosions, cells can be designed with safety vents, which may be either one-time vent mechanisms that disable the cell after use, or may allow multiple venting events. The Sony cell safety vent design is a one-time destructive mechanism (Ozawa and Yokokawa 1993: Figure 2).

Safety in Workplace Procedures

Industrial hygiene practices can mitigate the workplace hazards of possible lithium ion battery materials. In the case of materials for which a PEL has been established, OSHA requires such mitigation. For example, dust inhalation is a possible route of exposure for many materials described above. However, material handling procedures to minimize dust dispersion, dust collection, and monitoring systems can limit and monitor worker exposure to hazardous dusts. If monitoring indicates concentrations of a dust that could violate a PEL, workers may be required to wear dust masks. Material handling procedures, dust collection, and monitoring systems are in use among battery material suppliers. For example, Hall Chemical applies these measures in its work with cobalt, nickel, and manganese.

Safety Status

Lithium ion EV batteries have not yet been made, so this discussion will describe safety tests of lithium ion cells manufactured by Sony and SAFT. Sony and the U.S. Army have conducted the safety tests described here.

Sony Tests

Sony published the results of tests on 14500 (14 mm x 50 mm) and 20500 (20 mm x 50 mm) size cells. Tests included cycling performance, discharge capacity between -20° and 60°C, crush, nail penetration, overcharging, and short circuiting. No hazardous behavior during normal cycling was reported. No fires occurred during abuse tests.

Relevant to the previous discussion of electrolyte containment, Sony's nail penetration tests found that five of the 20 Sony cells leaked electrolyte when tested after extensive cycling, compared to 19 of the 20 cells tested before cycling. Similar results, which show less leakage after cycling, were obtained for the crush test (Ozawa and Yokokawa 1993: Tables 3 and 4):

Table 4. Crush Test

Cell	**Number of Cells**	**Test Results**					**Remarks**
		Leakage	**Smoke**	**Flame**	**Eruption**	**Eruption and Fire**	
Initial	20	20	20	0	0	0	
600th Cycle	5	5	0	0	0	0	
1200th Cycle	5	5	0	0	0	0	Maximum Temperature 78°C~98°C

Test results of crush test of 20500 size cell (Source: Ozawa and Yokokawa 1993: Table 3)

During Sony's safety tests, researchers measured temperature increases as follows:

Test	Maximum Temperature (°C)
Crushing	78-98
Nail penetration	77-105
Overcharging	<70
Short circuit	150

Table 5. Nail Penetration

Cell	Number of Cells	Test Results					Remarks
		Leakage	Smoke	Flame	Eruption	Eruption and Fire	
Initial	20	19	1	0	0	0	
600th Cycle	5	5	0	0	0	0	
1200th Cycle	5	5	0	0	0	0	Maximum Temperature 77°C~105°C

Test results of nail penetration of 20500 size cell (Source: Ozawa and Yokokawa 1993: Table 4.)

The temperatures increase because the tests allow uncontrolled current flow through cell materials. In a battery, a short-circuited cell that heated to 150°C (Ozawa and Yokokawa 1993: Table 6) could damage adjacent cells. The lower maximum temperatures reached during the crushing, nail penetration, and overcharging tests (Ozawa and Yokokawa 1993: Tables 3 to 5) are less likely to damage adjacent cells. As described in Safety in Battery Design, temperature-sensitive separators that stop electrochemical reactions when heated can help limit temperature increases. U.S. Army tests suggest that such separators are effective.

Safety tests were performed on cycled and uncycled cells. During overcharging and short-circuit tests, the temperature of cycled cells increased similarly to uncycled cells. For crushing and nail penetration tests, comparative temperature data for cycled and uncycled cells were not reported. No report of state of charge was included in the test descriptions (Ozawa and Yokokawa 1993:3, Figures 15 and 16, Tables 3 and 4). State of charge is an important consideration, because electrode materials in charged cells are generally more reactive than in uncharged cells. Reactivity of positive and negative electrode materials is considered in Intrinsic Material Hazards.

Smoke was produced during nail penetration, crush, and short-circuit tests, but not during the overcharge test (Ozawa and Yokokawa 1993:3, Tables 3 to 6). The maximum temperature during the overcharge test was lower than during the other tests. The smoke likely comes from either the sealant, a resin or plastic material, or from the separator (Small 1995).

Army Tests

The U.S. Army tested Sony cells during charging, discharging, and storage conditions intended to represent normal use (not abuse) conditions. Charge and discharge temperature, current, and voltage were varied. Test temperatures ranged from -30° to 50°C during charging and from -20° to 50°C during discharging. Storage test temperatures were 45° and 50°C. Charging regimes were a constant potential charge with 1.1-A and 4.1-V limits, and constant current charge with three steps, 700 mA with a 3.9-V limit, 200 mA with a 4.1-V limit, and 50 mA with a 4.25-V limit. Constant current and pulsed discharge tests were performed. Constant current discharge tests used currents of 0.5, 1, 2, and 3A to 2.5V. Pulsed discharge tests used 5-A and 4.5-A, 5-s pulses with 25-s pauses to a 2.5-V limit. The conclusion of this study of normal use conditions was that the Sony cells exhibit "safe operation" (Au and Sulkes 1993:9).

The U.S. Army has also performed abuse tests on SAFT LION Fat D cells. A short-circuit test on this type of cell with a simple polypropylene separator caused a temperature increase to at least 110°C. In contrast, a short-circuit test on the same type of cell with a shut-down separator caused a temperature increase to only 60°C (Au and Sulkes 1995).

Conclusions

Normal operating temperatures of lithium ion cells do not present significant burn hazards, and normally operating cells do not expose the user to material hazards. Material hazards considered in this chapter are unlikely to apply to all commercialized lithium ion systems. Because the exact composition of future batteries is unknown and information about battery materials is sometimes proprietary, a definitive presentation of material hazards is not possible. Some possible lithium ion battery materials are toxic, carcinogenic, or could undergo hazardous chemical reactions that produce heat or gases. Toxic materials include lithium, nickel compounds, arsenic compounds, fluorides, and DME. Carcinogenic materials include nickel compounds, arsenic compounds, and (possibly) cobalt compounds, copper, and polypropylene. The negative electrode, when lithiated, could cause hazardous reactions.

Intrinsic material hazards can be mitigated through cell and battery design and workplace practices. Cells and batteries can be designed to mitigate these hazards by containing the battery materials and reducing the chance of a hazardous chemical reaction. Thermal management of the battery system, electrical protection, containment of battery materials, and venting of gases can reduce the hazards of a lithium ion system. Workplace practices can mitigate occupational hazards of these materials. However, safety testing of any forthcoming EV battery should include tests of battery behavior during normal use and under abuse conditions.

Environmental Issues for Lithium Ion Batteries

Environmental regulations, along with minimization of waste during the full fuel life cycle of lithium ion batteries, are important considerations in developing any new battery technology. This chapter presents an overview of some regulations and waste minimization issues that may affect the lithium ion system's introduction. A full life-cycle assessment of environmental impacts of lithium ion batteries is not attempted here. Such an assessment would aid the evaluation of lithium ion batteries for EVs.

Environmental Regulation of Lithium Ion Battery Manufacturing

Lithium ion battery manufacturing processes will probably generate water and air emissions and solid waste. Environmental regulation of these effluents occurs at the federal, state, and local levels. Some federal regulations will be considered here. U.S. Environmental Protection Agency (EPA) regulations that pertain to these by-products were prompted by the following legislation: the Clean Water Act (CWA), Clean Air Act Amendments (CAAA), and the Resource Conservation and Recovery Act (RCRA). These acts are summarized below, with reference to their impact on lithium battery manufacturing.

Clean Water Act

There are 65 categories of "priority pollutants," including at least 126 toxic pollutants (Arbuckle et al. 1993:219-220). If discharged, they are subject to regulation under the CWA. These regulations affect 34 types of industries (Arbuckle et al. 1991), which include more than 700 subcategories.

Substances that could be used in lithium ion battery manufacturing and are listed as priority pollutants include nickel, arsenic, copper, and associated compounds. Substances that could be included in lithium ion batteries are listed in Table 1.

Battery manufacturing is regulated for toxic discharges; lithium battery manufacturing is listed as a subcategory (40 Code of Federal Regulations [CFR] §461.50). Although manufacturing operations of lithium batteries that have lead iodide or iron disulfide cathodes are the only ones specifically referred to in the CFR, EPA could also evaluate lithium ion battery manufacturing operations.

The National Pollutant Discharge Elimination System (NPDES) requires facilities to obtain permits to start or continue any discharge of pollutants to surface waters. Facilities must describe the nature and circumstances of any anticipated discharge when they apply to EPA for a permit. Direct discharges from manufacturing facilities and any storm water runoff from industrial facilities require an NPDES permit. Industrial dischargers to publicly owned treatment works (POTWs) are required to comply with the general pretreatment standards in 40 CFR part 403, and may be required to comply with industry-by-industry standards (categorical limits). Industrial discharge permits are issued by the POTW to industrial dischargers that discharge into the POTW's system.

Publicly owned treatment works are subject to the permit requirement of NPDES. According to EPA regulations, a discharge to a sewage system not connected to an operable treatment works is subject to the NPDES program, but a discharge to a POTW that can meet its effluent limits is exempt (40 CFR §122.3[c]). Industrial dischargers to POTWs are required to comply with general pretreatment standards (40 CFR part 403). General pretreatment standards focus on preventing the discharge of pollutants into POTWs that interfere with their operation, or pass through. These standards include prohibiting the introduction into POTWs of pollutants that:

1. Create a fire or explosion hazard

2. Have a pH less than 5.0, unless the POTW is designed for such low pH levels (although the lower pH limit is established in the regulation, the POTW decides the acceptable lower pH limit in the effluent it receives)

3. Emit toxic gases, vapors, or fumes in quantities that may cause acute health and safety problems.

Some substances (other than lithium and hydrogen[1]) that could be contained in lithium ion batteries may be subject to general pretreatment standards. For instance, the organic liquids used in the electrolyte are flammable, and the lithium metal oxides react with water to give lithium hydroxide (LiOH). The pH of LiOH may increase the discharge pH beyond the acceptance level set by the POTW.

Clean Air Act

The Clean Air Act Amendments of 1990 list 189 substances as hazardous air pollutants (HAPs) (CAA §112[b]) that must be regulated. Any stationary source that emits more than 10 tons/year of any regulated substance, or 25 tons/year of any combination of substances, is a major source and is subject to regulation under the major source program. The EPA published a list of all major source categories and subcategories of HAPs to be regulated under CAA §112 (Federal Register 1992a). Since then, EPA drafted a schedule for promulgating emission standards, specifying when each listed source category will be regulated (Federal Register 1992b).

Battery manufacturing is listed as a major source category. Hazardous air pollutants that may be used in lithium ion battery manufacturing are manganese, nickel, cobalt, and arsenic (and their compounds). Lead-acid battery manufacturing is now the only battery manufacturing process listed as a major source subcategory. No specific Maximum Achievable Control Technology standard has yet been established; however, battery manufacturing will be subject to the general permit requirements under Title V of the 1990 CAAAs.

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[1] Hydrogen evolved from the lithium and water reaction is an explosion hazard.

Hazardous air pollutants may not be the only air pollution generated during manufacturing of lithium ion batteries. If volatile organic compounds, nitrogen oxides, carbon monoxide, or fine particulates are generated during manufacturing, the facility may have to comply with applicable nonattainment pollutant requirements specified in the State Implementation Plans. Each state is responsible for ensuring that the air quality within its borders is maintained at a level consistent with the national ambient air quality standard (NAAQS) program (CAA §107 and §110). The NAAQS's are designed to protect the public health, with a margin of error ("primary" NAAQS), and to promote public welfare ("secondary" NAAQS) (CAA §109).

Resource Conservation and Recovery Act

Section 1004(27) of the RCRA defines a solid waste as "any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant or air pollution control facility and other discarded material, including solid, liquid, semisolid, or contained gaseous materials resulting from industrial, commercial, mining and agriculture activities and from community activities." Solid or dissolved material in domestic sewage, irrigation return flows, or industrial discharges to surface water is not included in this definition. However, these "point sources" may require a permit under CWA §402.

Solid waste is considered hazardous and becomes subject to RCRA if EPA lists it as a hazardous waste in 40 CFR Part 261, Subpart D (if it has not been delisted) or if it is corrosive, flammable, reactive, or toxic (characteristically hazardous). For example, lithium and arsenic may be reactive and toxic, respectively, and therefore hazardous when discarded.

A mixture of a solid waste and a listed (hazardous) waste may also be considered hazardous. Such a mixture may qualify for an exemption (40 CFR § 261.3[a][2]). However, these exemptions do not apply when wastes are intentionally mixed. Such mixing may be interpreted as treatment and could require an RCRA permit (Arbuckle et al. 1993).

In 1984, RCRA amendments imposed waste minimization requirements on hazardous waste generators. The EPA defines *generator* to include any facility, operator, or person who first creates a hazardous waste, or first makes the waste subject to RCRA regulations. Generators must certify that they have a program in place to reduce the volume and toxicity of hazardous wastes as economically practicable. They must also select the method of treatment, storage, or disposal that minimizes the threat to human health and the environment (Hall et al. 1993). The Universal Waste Rule (also referred to as "Part 273") may, to expedite recycling, exempt generators and handlers of certain hazardous wastes from the RCRA hazardous waste handling and storage requirements.

Waste Minimization

Waste minimization is reducing hazardous waste as much as possible. It includes source reduction and recycling that results in reducing the total volume (or quantity), toxicity, or both, of hazardous waste.

Source reduction reduces or eliminates hazardous waste generation at the source. Recycling reuses or reclaims a material (40 CFR 261.1[c][7]). A material is reclaimed if it is recovered as a useful product or regenerated (40 CFR 261.1[c][4]). Source reduction and recycling/reclamation are discussed in the following sections.

Source Reduction

Hazardous wastes may be reduced in two ways: (1) Product substitution, in which a product (or technology) that creates less hazardous wastes replaces the existing product; and (2) Controlling the source during manufacturing by making changes in the input material, technology, or the procedure and institution.

Input material could be changed through purification, substitution, or dilution. For example, using $LiPF_6$ instead of $LiAsF_6$, in the electrolyte eliminates hazardous waste. The arsenic (which is toxic) in $LiAsF_6$ may be considered characteristically hazardous and subject to RCRA regulations when discarded.

Technology changes implemented to reduce waste include changing the process, equipment, layout, and operational settings. Additional automation and improving energy and water conservation may be implemented as source control measures.

Procedural or institutional changes may include altering process conditions such as temperature or pressure. Preventing spills, leaks, and other releases, and segregating hazardous and nonhazardous wastes are also important considerations when developing manufacturing processes or institutional operating practices (Kokoszka and Flood 1989).

Recycling and Reclamation

The best place to recycle, in most cases, is at the production facility. Wastes that are contaminated versions of the raw materials used in manufacturing the batteries are good candidates for on-site recycling. However, this type of recycling may not be feasible for lithium battery manufacturing if the recovered materials cannot be reused in the production process (for example, the level of purification needed may not be feasible), or too little waste is generated to make an in-plant recovery system cost effective.

When batteries reach their full life span, they will probably be sent to a recycling facility that specializes in the specific battery type. For instance, nickel-cadmium batteries may be sent to INMETCO, SNAM, SAVAM, or SAFT Nife. However, recycling and reclamation of lithium batteries are currently limited. Generally, disposal (after deactivation) of lithium compounds in an approved hazardous waste landfill such as BDT, Inc., is the mode of operation. Toxco in Trail, British Columbia, is the only known exception. It recovers lithium salts from the batteries to sell to the cement industry. More research is needed on processes for separating the lithium salts so they can be reused in batteries. Developing this type of process is important because of the expense of lithium salts.

Generically, the Toxco process involves the following steps:

1. Batteries are bathed in liquid nitrogen before shredding to reduce the lithium's reactivity[2]
2. C Shredded batteries are treated in an aqueous caustic solution
3. Insoluble casings and other materials are separated from the soluble lithium salt
4. C Magnetic casings are separated for recycling
5. Nonmetal casing and wiring materials are landfilled
6. C Lithium salts are built up in the caustic solution until they precipitate
7. C Salts are filtered out and sold.

(Beyke 1995; Charlton 1995)

A proposed process[3] to recycle and recover constituents in lithium ion battery systems is depicted in Figure 1. This is a four-part process:

1. Cools the batteries in a liquid nitrogen tank to reduce the reactivity of the lithium in the batteries
2. C Shreds the batteries in the shear shredder before they enter the alkaline solution tank
3 The lithium in the electrodes reacts with the water in the solution tank, producing lithium hydroxide and hydrogen
4. C The hydrogen generated in the lithium and water reaction burns.[4]

The hydrolysis of PC or EC, in the alkaline solution tank, in the presence of lithium ions, produces propylene glycol or ethylene glycol and Li_2CO_3 (a lithium salt). Other lithium salts are made during the hydrolysis of $LiAsF_6$ or $LiPF_6$, which produces LiF and Li_2AsO_4 or LiF and Li_3PO_4, respectively. The propylene and ethylene glycols—along with DEC, DMC, and DME—are flammable and will burn on the surface of the alkaline solution tank. All gases, fumes, and dust from the shredder and solution tank are sent to the scrubber before they are vented.

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[2] The lithium reactivity in lithium ion battery systems depends on the state of charge. In a fully charged lithium ion battery, the carbon negative electrode is filled with lithium ions and may approach the electrochemical potential of lithium metal.

[3] This process was derived from processes used at Toxco to recover lithium salts from lithium batteries and processes used to recover metals.

[4] In the Toxco process, the lithium metal on the surface of the tank ignites, initiating the combustion of the flammable materials. Lithium metal is more reactive than lithium ions, and another step may be necessary to ignite the flammable substances.

The lithium salt, from the hydrolysis of PC or EC, along with all other salts produced during the hydrolysis process in the alkaline solution tank, will be precipitated and recovered.[5] The metal oxides are insoluble and will also be recovered with the lithium salts. The lithium salts and the metal oxides may be separated at this point, depending on the market value of the metal. Aluminum, copper, and nickel-plated steel may also be recovered and recycled. Polyvinylidene fluoride is recovered with the lithium salts. Polypropylene and other low-value components will probably be landfilled (Charlton 1995).

The profitability of recovering the metal used in the positive electrodes is currently being assessed by manufacturers such as Sony. If these metals can be recovered economically, a number of processes to separate the metal from the waste stream may be investigated. The spent batteries might be sent to a secondary smelter to recover valuable metals such as cobalt (Small 1995). The lithium salts will not be recovered in this case. Other processes to recover valuable metals that warrant further investigation include electrolytic recovery and ion exchange. These processes are described in the following paragraphs.

The essence of electrolytic recovery is the oxidation-reduction reactions that take place at the surface of conductive electrodes (cathode and anode). The electrodes are submerged in a chemical agent, and a potential is applied. The metal ion is reduced to its elemental form at the cathode, and gaseous products such as oxygen may evolve at the anode. Dissolved species are oxidized at the anode (Freeman 1989). Depending on the plating potential of the metal, hydrogen may form at the cathode. The reduction potentials[6] for nickel and cobalt are higher than water's reduction potential. Hence, nickel and cobalt will plate out at the cathode during electrolysis in an aqueous solution, whereas lithium (in an aqueous solution) is not a good candidate for electrolytic recovery. Water is reduced at a higher potential than lithium; therefore, this metal will not plate out from an aqueous solution (Lide and Fredrickson 1995).

Ion exchange is an ion separation process. Metal ions are removed from the liquid in the ion exchange process. Other separation processes such as evaporation and reverse osmosis remove the liquid from the metal. Hence, ion exchange is usually more effective in treating waste streams with small quantities of metals. Another major advantage is that ion exchangers can purify and concentrate metals. Ion exchangers may be designed to be selective for specific metals. Such specially designed exchangers effectively remove low concentrations of toxic metal from a waste stream that contains high concentrations of nontoxic metal (Freeman 1989).

Plastics are and have been recycled in the automotive industry. For example, conversion of polypropylene (and other plastics) into molding compounds is a fully developed industry. The materials produced from this industry are used successfully to manufacture automotive components.

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[5] Recovered lithium salts (also includes $LiAsF_6$) produced from the hydrolysis of lithium hexafluoroarsenate may be classified as hazardous because of the toxicity of arsenic.

[6] Reduction potential indicates the direction and spontaneity (voltage) of an electrochemical reaction.

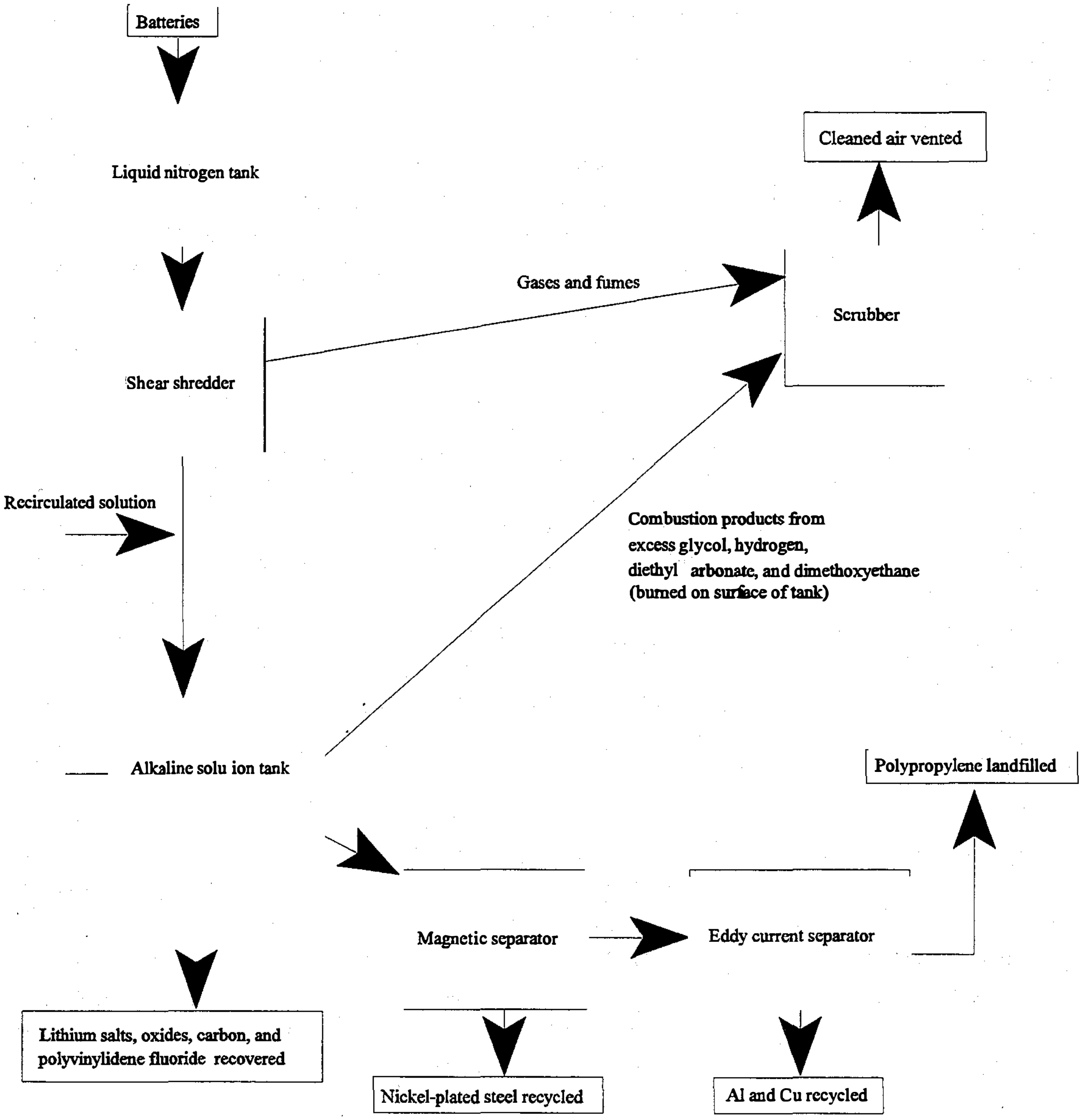

Figure 1. Potential lithium ion battery recycling process

Research in the plastics industry has emphasized reducing the costs of polymers and creating polymers that achieve specific economic and material property goals by alloying dissimilar materials. Compatibilization and reactive compounding technologies accomplish this alloying. These manufacturing techniques allow the manufacturing of compounds with the requested mechanical properties at a lower cost than was previously realized in polymerizing a new material.

Compatibilization and reactive compounding technology can be used to recycle and add value to the plastics contained in the lithium ion battery system. As an example, value can be added to polypropylene by compatibilizing it with glass-filled nylon 66 from radiator end tanks. The compound created displays qualities typical of engineering resins (Staniulis 1994).

Recommendations and Conclusions

Environmental regulations must be considered in developing any new battery technology. Lithium ion battery manufacturing processes may produce water and air emissions and solid waste. The Clean Water Act, CAAA 1990, and RCRA are some pieces of legislation that prompt applicable EPA regulations.

Source reduction is more environmentally desirable than recycling and should be explored before resorting to recycling. However, source reduction is not always feasible, and recovery and reclamation might be the only alternatives. Recovery or reclamation of lithium ion battery systems may be easier if RCRA Subtitle C regulations do not apply. Hence, the desirability of using $LiAsF_6$ is low: the arsenic might be considered a characteristically hazardous waste because of its toxicity.

Although lithium salts can be recovered for reuse in the cement industry, further research is needed to identify a recovery process that would make their reuse in batteries economically feasible. Such a process would be a valuable contribution to the economic viability of the batteries, because the lithium salts are expensive.

The volume of metals and plastics that may be recovered from batteries will increase as EVs become more common. The profitability of recovering metals that may be used in the lithium ion system is being evaluated by manufacturers (such as Sony). Sony is considering sending spent batteries to a secondary smelter to recover valuable metals (Small 1995). Processes to recover valuable metals that may be investigated further include electrolytic recovery and ion exchange.

Instead of landfilling plastics, consideration should be given to recycling. The automotive and plastics industries have invested considerable time to develop the means to enhance the value of plastics to make the effort of recycling worthwhile. Economically feasible industrial processes to recycle some plastics have already been developed, but further research will be needed to develop a commercial process for lithium ion EV batteries.

This chapter does not provide a full life-cycle assessment of environmental impacts of lithium ion batteries. Further study to assess life-cycle environmental impacts is recommended.

Shipping Requirements for Lithium Ion Batteries

Introduction

This chapter examines the shipping regulations that govern the transportation of lithium ion batteries because of the hazards that these batteries (or their cells) may pose in transportation. Regulations at both the domestic and international levels prescribe requirements for shipping any substance or article considered to be a "hazardous material"[7] on the basis of meeting the definition for one or more "hazard classes" established under those regulations. The basic requirements of the domestic hazardous materials transportation regulations are fundamentally consistent with those in the major international transportation regulations. Therefore, this assessment will primarily review the applicability of the domestic regulations to the transportation of lithium ion batteries, with the understanding that (subject to confirmation by the appropriate regulatory authorities), the same basic principles would apply to international transport.

The lithium ion battery is a developing technology that may employ different chemistries and pose differing associated hazards in transport. Therefore, conclusions regarding the specific requirements and conditions that would apply to the transport of these batteries cannot be drawn at this time. Accordingly, this assessment will outline the principles that may apply in determining, based on battery configuration and the possible hazards, how these types of batteries would be regulated in transport.

The fundamental goal of all hazardous materials transport regulations is twofold: (1) to identify articles or substances that pose an "unreasonable" risk to health, safety, and property when transported in commerce; and (2) to prescribe measures to control these risks to ensure the article or substance is transported without exposing the public to unreasonable risk. Materials that pose an unreasonable risk in transport have been identified by defining the types of hazards of concern in transport. Substances or articles that exhibit these characteristics are deemed hazardous in transport and therefore subject to regulation. Such hazards include, but are not limited to, explosiveness, flammability, toxicity, corrosiveness, reactivity with water, and oxidizing potential. A scheme of hazard classification has been elaborated under which a specific "hazard class" is provided into which substances that pose such risks must be classified for transport.

To promote uniformity in hazardous materials transport requirements at the global level and between the various modes of transport, regulatory systems based on recommendations developed by the United Nations (UN) have evolved. These recommendations are prepared by the UN Committee of Experts on the Transport of Dangerous Goods, and are published in a two-volume set entitled *Recommendations on the Transport of Dangerous Goods*. The UN Recommendations form the basis not only of the international air and sea transport requirements, but also of the domestic hazardous

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[7] Note that the term *hazardous material* is normally employed in U.S. domestic regulations, whereas the term used in most international regulatory standards to describe such materials is *dangerous goods*.

materials transport regulations. A fundamental consistency between these regulations exists—not only in identifying those substances and articles deemed to pose a risk in transport, but also in establishing requirements that apply to the transport of such substances and articles.

The details of the various international and domestic regulatory standards may differ in certain respects, but the basic principles and measures that ensure transport safety are the same. Certain basic features exist that are common to all regulatory systems. For example, all systems contain similar definitions that prescribe characteristic properties of materials considered to constitute a hazard in transport. These definitions must be applied to identify materials or articles subject to regulation in transport. For substances and articles that meet one or more hazard class definitions, each regulatory system imposes the following basic responsibilities on the person offering the material for transport or transporting the material:

1. Maintain minimum packaging standards

2. C Mark and label packages to identify the substance or article and nature of the hazard

3. Include required information on transport documentation to identify the substance or article transported, its hazard, the quantity being shipped, and (in some cases) the steps to take in the event of an incident involving the material

4. Include a signed certification stating that all applicable requirements have been fulfilled

5. C Depending on the mode of transport involved (rail, highway, vessel, aircraft), comply with specific requirements for loading, handling, and carrying the goods (identify vehicles that contain dangerous goods, segregate incompatible goods, etc.).

In addition, U.S. Department of Transportation (DOT) Hazardous Materials Regulations and major international transport regulations contain specific requirements for training all individuals involved with the offering for handling or transporting hazardous materials. This includes, but is not limited to, persons involved in classifying hazardous materials, packaging, marking, labeling, and preparing shipping papers, and any other preparation of a consignment for shipment. This assessment assumes that persons engaged in the transport of lithium ion batteries will have received the required training in the Hazardous Materials Regulations. In addition, because the lithium ion battery technology is still in its infancy, the design of batteries and cells, the materials they contain, and the nature of their hazards, are subject to change. For these reasons, no attempt is made to address all details of the regulations that apply to the transport of these devices. Instead, this assessment will focus on the principles that may apply in determining (based on battery configuration and the hazards possibly posed) how various types of lithium ion batteries would be regulated in transport.

Background on Domestic Transportation Requirements

Introduction

The offering for transportation and transportation of hazardous materials within the U.S.—either for domestic or international transport—is governed by the DOT Hazardous Materials Regulations. These regulations are codified in 49 CFR, 100–180, and apply to transportation within the U.S., including its territorial waters and airspace, by any mode of transportation—highway, rail, vessel, or aircraft. Under these regulations, a *hazardous material* is defined as any "substance or material . . . which has been determined by the Secretary of Transportation to be capable of posing an unreasonable risk to health, safety, and property when transported in commerce . . . "

Materials and Devices Forbidden in Transportation

Before any chemical, device (including any type of battery), or any other product may be offered for transport or transported in the U.S. (for either domestic or international shipment), the person offering the material or device must determine that it does not pose an inherently unacceptable risk in transport. Materials that pose such risks are referred to as "forbidden" materials in the DOT regulations. Section 173.21 of the DOT regulations provides a qualitative description of the types of materials considered to pose such inherent risks in transport as to be forbidden from transport. Forbidden materials include:

1. Electrical devices that may create sparks or generate a dangerous quantity of heat, unless packaged to preclude such an occurrence

2. Packages that emit flammable gas or vapor released from a material not otherwise considered a hazardous material[8] that is likely to create a flammable mixture with air in a transport vehicle.

Batteries that pose such risks (as packaged for transport) would be unacceptable for transport. Examples would include charged batteries in which short circuits could result in the generation of dangerous quantities of heat, unless packaged to prevent such an occurrence (such as by protecting terminals from short circuit), or batteries that can evolve dangerous quantities of flammable gases. No quantitative criteria are provided in the regulations to define "dangerous" quantities of heat or gas, so a subjective judgment must be made based on the packaging and manner of transportation, and the conditions likely to be encountered in transport.

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[8] An example of a material that emits flammable gas or vapor that is considered a hazardous material would be a flammable liquid (such as acetone). This material is considered a hazardous on the basis of meeting the definition for Class 3 (flammable liquid), so it is not a "forbidden" as a result of its ability to give off flammable vapors.

Determining Applicable Shipping Requirements

If a lithium ion battery or cell has been determined not to be a forbidden material, the battery or cell may be offered for transport, and transported, provided all applicable requirements of the DOT regulations are satisfied.[9] Under the regulations, the person offering an article or substance for transportation must determine whether the material is hazardous and subject to regulation in transport and, if so, which requirements apply to its transport. These determinations are made according to various procedures and criteria presented in Parts 172 and 173 of the regulations.

Part 172 of the DOT Hazardous Materials Regulations contains a table that lists materials considered hazardous in transportation. In addition to hazardous substances (liquids, solids, and gases), the table lists a number of articles or devices (for example, certain types of batteries) that contain hazardous materials and are considered hazardous for transport. For each substance or article, the table indicates the hazard class, provides a four-digit identification number (usually prefaced by the letters "UN"), refers to a section in the regulations that prescribes the required packaging, and provides other information such as required hazard labels and indications of whether, and in what quantities, the listed material may be transported. The regulations require the person offering the material for transportation to select the entry from this list that most closely describes the material to be transported and that is associated with the hazard class corresponding to the hazard posed by that material.

Part 173 of the regulations provides the definitions (including relevant tests and defining criteria) for the various hazard classes. If a material meets the definition of a hazard class, it is subject to regulation in transport, whether or not it is listed by name in the hazardous materials table. For such materials, the table contains generic listings based on the hazards presented by the material in question (for example, "Corrosive liquid, n.o.s.", "Flammable solid, n.o.s." or "Hydrides, metal, n.o.s."[10]). For each generic entry, the table refers the user to the sections in the regulations in which the applicable regulatory requirements are presented.

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[9] Batteries not meeting these requirements may only be transported under an "exemption" issued by the DOT. An exemption is a document permitting the transport of a hazardous material either not allowed under the Hazardous Materials Regulations, or under conditions different from those specified in the regulations. An applicant for an exemption must demonstrate to the satisfaction of DOT that the proposed method of transport provides a level of safety equivalent to that afforded by the regulations. Exemptions are issued for a maximum period of validity of 2 years, after which time the exemption holder must apply for renewal. If renewal is not applied for, or is not granted by DOT, the exemption expires at the end of its specified term of validity.

[10] The abbreviation "n.o.s." stands for "not otherwise specified." When a material that meets the definition of a hazardous material is not listed by name in the hazardous materials table, the regulations provide that the material must be transported in accordance with the requirements applicable to the "n.o.s." or generic entry in the table that corresponds to the specific hazard class, packing group, and subsidiary hazard (if any) of the material.

Factors Affecting Determination of Applicable Requirements

A first step in determine whether, and in what ways, lithium ion batteries are subject to the DOT regulations in transport, requires evaluation of the battery (and the materials it contains) under the hazard class definitions in Part 173 of the regulations to establish whether the battery, or any material it contains, is hazardous and if so, to which hazard class it is assigned. Once this is determined, the entry that most closely describes the battery, including its associated hazard class (which must correspond to the hazards posed by the battery), can be selected. This in turn provides the references to the specific regulatory requirements applicable to the transport of the batteries. The entry/hazard class that would most closely describe lithium ion batteries, and whether a particular battery is considered hazardous, may vary considerably and depend on a variety of factors, including:

1. The chemistry of the electrolyte associated with the battery design, and the extent to which "free" electrolyte may be present (i.e., whether the battery may be considered "dry")
2. Whether the battery has been cycled
3. For previously cycled cells, the state of charge.

These factors may apply to a particular battery independently, or in a myriad of combinations that lead to a variety of possible "solutions" to the problem of determining which regulatory requirements apply to the transport of that battery. The possible effects of each factor on this process are considered in greater detail below.

Chemistry/Quantity of Electrolyte

The electrolyte used in lithium ion batteries consists of an organic solvent into which a lithium salt is dissolved. The organic solvent would typically consist of a cyclic carbonate, such as EC, to which DEC, DMC, or DME may be added. Lithium salts for commercial use include $LiPF_6$, possibly $LiBF_4$, and organic salts. To properly identify the possible hazards of the lithium ion battery as a whole, the hazard(s) posed by the electrolyte must be considered.

Under the DOT regulations, the hazard of a mixture of materials (such as this electrolyte) is determined on the basis of the hazard properties of the mixture, not on the hazards of its individual components. The presence of a hazardous material as a component does not necessarily result in the mixture's being considered to pose the hazard of that component. For example, a mixture that contains nonhazardous materials with only a low concentration of a substance classified as a poison under the DOT regulations, would be considered a poison only if the toxicity of the mixture was high enough to meet the defining criteria in the DOT regulations.

According to the DOT regulations (see §173.120), liquids with a flashpoint at or below 60.5°C are generally classified in Class 3 (flammable liquids).[11] The flashpoint of the liquids that may compose the electrolyte solvent range from 19°C (for DEC) to 145°C (for EC), the latter being well above the upper flashpoint limit for classification as a flammable liquid under the DOT regulations. Accordingly, depending on the organic solvents used in the electrolyte, and, if more than one, on the concentration of each, the flashpoint of the electrolyte may be at or below 60.5°C, in which case the electrolyte would be considered a flammable liquid under the DOT regulations. On the other hand, if the flashpoint of the electrolyte exceeds 60.5°C, the electrolyte would not meet the DOT definition of a flammable liquid.

The lithium salt dissolved in the solvent may also contribute to the hazards of the mixture. For example, $LiAsF_6$, and, to a lesser extent, $LiPF_6$, may satisfy the definition in Part 173 of the DOT regulations for classification in Division 6.1 (poison). Therefore, depending on the concentration of this salt in the electrolyte, the electrolyte itself may meet the defining criteria for a poison.[12] Furthermore, determination that the electrolyte meets the DOT defining criteria for a poison may be in addition to meeting the definition of a flammable liquid, as described above. Similarly, the electrolyte may meet the defining criteria for Class 8 (corrosive).[13]

Consequently, under the DOT regulations, the possibility exists that electrolyte may be considered either nonhazardous, or to be a flammable, poison, and/or corrosive liquid. Which hazard, if any, the electrolyte poses may directly affect the transport requirements applicable to the battery.

Even though the electrolyte may pose hazards, the absence of "free" electrolyte in the battery may alter the extent to which the hazards need be taken into account in determining the transport requirements applicable to the lithium ion battery. For example, in the case of more traditional battery technologies (e.g., lead-acid batteries), where the electrolyte meets the definition of a hazardous material, DOT has determined that the hazard of the electrolyte need not be considered in assessing the overall hazards of the battery when, because the electrolyte is either in a gel form or

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[11] For transportation by rail or highway only, a flammable liquid with a flashpoint at or above 38°C (100°F) need not be considered a hazardous material provided it does not meet the definition of any other hazard class (poison, corrosive, etc.) and that not more than 450 liters (119 gallons) of the liquid is contained in the package in which the liquid is to be transported. (see §173.150)

[12] The defining criteria for Division 6.1 (poison) materials in § 173.132 of the DOT regulations are based on toxicity as determined by animal testing (e.g., the oral LD_{50} (rat) value). In the case of liquids, the defining criteria consider three separate routes of exposure: oral, dermal, and inhalation of vapors and mists.

[13] Under the defining criteria for Class 8 (corrosive) materials, as presented in § 173.136 of the DOT regulations, a material may be judged corrosive based either on its ability to cause full thickness destruction to intact skin (as determined by testing albino rabbits according to prescribed procedures) or on its rate of corrosion to steel or aluminum.

is contained in the battery separators and electrodes (i.e., the battery is of a "starved electrolyte" design), it meets the criteria of a "dry" battery. In a number of letters issued by DOT[14], a dry battery has been defined on the basis of the following criteria:

> If . . . the batteries are of such a design that no flow of battery fluid would occur if the batteries were ruptured or cracked, and there is no free liquid, we would consider the batteries to be "dry" . . . .

Based on these precedents and on informal discussions with representatives of DOT, hazards associated with the electrolyte in a lithium ion battery may not need to be considered in assessing the overall transportation hazard if it can be considered a dry battery. While DOT may consider developing specific dry battery criteria for lithium ion batteries, for this assessment, a dry lithium ion battery is one that satisfies the previously established criteria.

The specific chemistries of the electrolytes that may be used in lithium ion batteries vary considerably. The possible hazards posed by those electrolytes, as determined by the definitions of the various hazard classes in Part 173 of the DOT regulations, vary also. An electrolyte may be nonhazardous (i.e., may not meet the defining criteria for any hazard class), or may meet the definition of one or more hazard classes, such as Class 3 (flammable), Division 6.1 (poison) or Class 8 (corrosive). However, even if the electrolyte is considered hazardous, the hazards of the electrolyte need not be considered in evaluating the overall hazard posed by the battery in transport if the battery meets the criteria for a "dry" battery.

Uncycled Batteries

Substances which may, in contact with water, become spontaneously flammable or evolve dangerous quantities of flammable gas, are generally considered hazardous for purposes of transport, and would be classified in Division 4.3 (dangerous when wet material) under the DOT regulations.[15] As a result, materials such as lithium metal and lithium metal alloys are, by definition, deemed hazardous in transport and subject to those regulations. However, the lithium ion battery may not pose this type of hazard if transported as fabricated and before being cycled.

For purposes of this assessment, an "uncycled" battery is one in which a newly fabricated carbon electrode has not been lithiated. If the non-lithiated carbon electrode were exposed to water, no flammable or poisonous gases would be evolved. Because carbon in the form used in the electrode

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[14] For example, letter dated Oct. 31, 1990, from Mr. E.T. Mazzullo of DOT to Mr. C.E.Unser of Fire Control Instruments, Inc.

[15] Specific criteria for classifying of substances in Division 4.3 (dangerous when wet) are presented in § 173.124(c) of the DOT regulations. A material is considered to pose a hazard of a Division 4.3 material when, on contact with water, the material evolves a flammable or toxic gas at a rate greater than one liter per kilogram of material, per hour, when tested in accordance with a prescribed procedure.

is not considered a hazardous material, even assuming that small amounts of additives such as boron or boron compounds may be present in the electrode, the carbon electrode would pose no hazard subject to regulation in transport. To assess the overall hazard posed by a battery in transport, no contribution need be associated with the carbon electrode of an uncycled battery. Because such a battery would be uncharged, it cannot pose any electrical hazard and could not be a forbidden material owing to possible risk of generating sparks or dangerous quantities of heat or gas.

Cycled Batteries

For purposes of this assessment, a "cycled" lithium ion battery is one in which the carbon electrode has been lithiated as a result of subjecting the battery to at least one charging cycle. As a result of the presence of lithium in the carbon matrix, on contact with water, the lithiated carbon electrode would probably evolve flammable gas (hydrogen) in much the same manner, and to much the same degree, as expected of the lithium metal or alloy used in conventional lithium batteries. Once lithiated, the carbon electrode would probably be considered a hazardous material according to the DOT regulations. In some cases small quantities of lithium metal have been deposited in the carbon electrodes of batteries after repeated cycling. Such deposits would further contribute to the possibility that the carbon electrode in cycled batteries would be considered hazardous for transport.

Once a lithium ion battery has been charged, the carbon electrode may never be rendered nonhazardous, because it is unclear whether sufficient lithium can be removed through discharging so that the electrode is, for all practical purposes, nonlithiated (as when initially fabricated). This is particularly true if enough lithium metal has been deposited to materially enhance the capability of the carbon electrode to react with water to evolve hydrogen. Nevertheless, assuming discharging could remove an amount of lithium sufficient to render the carbon electrode incapable of evolving hydrogen on contact with water at a rate necessary to result in classification as a Division 4.3 material, a previously cycled battery could, in principle, be considered equivalent to an uncycled battery.

Impact of Factors on Shipping Requirements

Depending on the extent to which each factor described above relates to a specific type of lithium ion battery, various conclusions are indicated about which regulatory requirements apply to transport. The following describes some situations most likely to occur when assessing the transport requirements for various types of lithium ion batteries. Each case assumes that it has been determined that the battery is not a forbidden material.

Case 1: Uncycled, "dry" battery. If there is no free electrolyte, such that the battery meets criteria for a "dry" battery, this case applies. The nonlithiated carbon electrode is not considered hazardous, and any hazard associated with the electrolyte need not be considered in assessing the overall hazard it poses, so the battery need not be considered hazardous, and would not be subject to the provisions of the DOT regulations in transport.

Case 2: Uncycled wet battery. If there is free electrolyte, such that the battery does not meet criteria for a "dry" battery, this case applies. The nonlithiated carbon electrode does not contribute to the overall hazard it may pose, so a determination of whether and how the battery is subject to regulation depends on the possible hazards of the electrolyte. The following two possibilities occur in this regard:

1. If the electrolyte does not meet the definition of any hazard class specified in the regulations, (is not flammable, corrosive, poison, etc.), the battery need not be considered hazardous, and would not be subject to the provisions of the DOT transport regulations

2. U If the electrolyte meets the defining criteria for one or more hazard classes specified in the DOT regulations, the battery could be regulated in accordance with the requirements applicable to the most appropriate hazardous materials table entry associated with the hazard class of the electrolyte. For example, if the electrolyte meets the definition of:

    a) Class 3 (flammable liquid), the requirements applicable to the transport of the battery would be those associated with the hazardous materials table entry:

        Flammable liquid, n.o.s., Class 3, UN 1993

    b) Division 6.1 (poison), the requirements applicable to the transport of the battery would be those associated with the more appropriate of hazardous materials table entries:

        Toxic liquid, organic, n.o.s., Division 6.1, UN 2811; or
        Toxic liquid, inorganic, n.o.s., Division 6.1, UN 3287.

Case 3: Cycled battery, fully discharged state. For purposes of this example, "fully discharged state" means the battery has been discharged to an extent that:

1. All or most of the lithium has been removed from the carbon electrodes and are therefore incapable of evolving hydrogen on contact with water at a rate necessary to result in classification as a Division 4.3 material

2. There is insufficient stored electrical energy in the battery to pose a significant hazard in transport, such as by a dangerous evolution of heat or gas as a result of internal or external short circuit.

Under these conditions, a previously cycled battery in a fully discharged state could, in principle, be considered equivalent to the uncycled batteries described above. That is, if it meets the criteria for a "dry" battery, or if not, when the electrolyte does not meet the definition of any hazard class specified in the regulations, the battery need not be considered hazardous. If it is not a "dry" battery, and the electrolyte meets the defining criteria for one or more hazard classes specified in the DOT regulations, the battery would be subject to regulation in accordance with the requirements applicable to the most appropriate hazardous materials table entry associated with the hazard class of the electrolyte.

*Case 4: **Cycled battery, charged state***. In this case, the lithiated carbon electrode evolves hydrogen on contact with water at a rate sufficient to meet the defining criteria for Division 4.3 and there is sufficient stored energy in the battery to pose a significant hazard in transport (i.e., the battery is not in a fully discharged state). This case poses the highest level of uncertainty for determining the applicable regulatory requirements in that the regulations do not specifically address the transport of lithium ion batteries that pose these types of hazards. In this connection, the two basic regulatory options described below appear to be available as a basis upon which to establish requirements for transporting lithium ion batteries.

> *Option 1*. Transport the lithium ion battery under the provisions applicable to the existing hazardous materials table entry:

Lithium battery, Class 9, UN 3090

This entry and the associated requirements were developed to provide for the safe transport of the more conventional lithium battery technologies (i.e., batteries that contain lithium metal or alloy), so the transport requirements may not in all respects be appropriate for lithium ion batteries. In particular, the quantities of lithium or lithium alloy allowed in a cell or battery are considered too low for larger batteries of the type envisioned for EV applications. In addition, a comprehensive testing regime, which may not be appropriate or necessary for lithium ion batteries, must be carried out to qualify batteries for classification and transport under this entry. Nevertheless, use of this entry would provide for a basic hazard classification and shipping description under which lithium ion batteries could be transported. In addition, the regulations provide that DOT may, at its discretion, approve the transport of lithium batteries that do not meet the specific test requirements and other limitations associated with the lithium battery entry.

> *Option 2*. Seek amendments to the DOT regulations, or a DOT exemption, to provide suitable transport for this category of lithium ion battery. Such an amendment could use the existing lithium battery entry, but provide alternative tests or criteria to govern the process of determining the suitability of lithium ion batteries for transport under that entry, as well as packaging and other requirements specifically tailored to lithium ion batteries. Alternatively, a completely separate hazardous materials table entry and UN number could be requested, and associated transport requirements added to the regulations, which would take specific account of the hazards and characteristics of lithium ion batteries.[16]

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[16] If either course of action were ultimately pursued, it may be advisable that the new or revised regulations or exemption apply to the transport of *any* lithium ion battery subject to regulation in transport, not only to those posing the combination of hazards described in this case. This would promote greater consistency in relation to the transport of various

To justify different regulatory treatment for lithium ion batteries compared to batteries that contain lithium metal or alloy, DOT would have to be satisfied that lithium ion batteries pose a significantly lesser, or different, hazard in transport than do batteries that contain lithium metal or alloy. Of key interest in this regard would be whether the lithiated carbon electrode is significantly less reactive on contact with water than is lithium metal. Research on the reactivity of lithiated carbon electrodes at various states of charge is anticipated. In addition, information that demonstrates any other differences in hazard between lithium metal and lithium ion batteries would have to be developed and made available to DOT. If such information indicates that the hazard posed by lithium ion batteries in transport is inherently different, or significantly less, than the hazard posed by batteries that contain lithium metal or alloy, a sound case could be made for implementing separate regulatory requirements to govern the transport of lithium ion batteries.

Packaging of Batteries and Cells

Once the appropriate hazardous materials table entry has been determined and the associated hazard class and identification number listed, that entry indicates the section in the regulations that prescribes the required packaging and provides other information such as required hazard labels and indications of whether, and in what quantities, the listed material may be transported. Other sections in the regulations provide the specific requirements for preparing the shipping papers that must be provided to the carrier with the shipment, and specify additional requirements such as those for marking packages and placarding the vehicles, rail cars, or freight containers in which the hazardous materials are transported. In general, compliance with the requirements associated with the relevant hazardous materials entry should pose no significant practical problems for transporting lithium ion batteries. The exception is for the packaging required by the regulations.

The packaging required for hazardous materials covered by the various hazardous materials table entries which may be appropriate for lithium ion batteries, would include packaging types such as metal or plastic drums, wooden, fiberboard, or plastic boxes, and a variety of other types of "nonbulk" packagings. In addition, the packagings for hazardous materials must meet certain construction, performance, and marking standards, as provided by DOT regulations. While use of packagings of the type, and meeting the standards required by the regulations would pose no serious practical difficulties for shipping cells for lithium ion batteries, the use of such packagings for transporting relatively large batteries that would be suitable for use in EV applications may not be practical. To address this problem, it may be necessary to obtain an exemption from DOT to authorize the use of alternative packaging more appropriate to large lithium ion batteries. For example, an exemption could be requested to allow large lithium ion batteries to be transported either unpackaged, or in protective packagings (such as crates) not subject to the performance requirements specified in the regulations. If provisions specific to the transport of lithium ion batteries are eventually incorporated into the DOT regulations, such packaging requirements and exceptions could be made a part of those provisions.

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types of regulated lithium ion batteries, and could provide a mechanism for incorporation into the regulations of packaging and other requirements specifically suited to large, lithium ion batteries such as would be used in EV applications.

International Sea and Air Transport Requirements

The international requirements applicable to the transport of hazardous materials (dangerous goods) by vessel are promulgated by the International Maritime Organization (IMO), and those applicable to international transport of such batteries by commercial aircraft by the International Civil Aviation Organization (ICAO). The IMO is a specialized agency of the UN responsible for developing standards and regulations to promote the safety of life and property at sea and to prevent pollution from ships. The IMO dangerous goods transport requirements are presented in a four-volume document entitled the *International Maritime Dangerous Goods Code* (or "the IMDG Code"). The requirements published by ICAO that govern the international air transport of dangerous goods are known as the *Technical Instructions for the Safe Transport of Dangerous Goods by Air* (or "the Technical Instructions"). Each regulatory standard is based on the UN Recommendations, but may contain additional quantity limitations and/or packaging or handling requirements for the particular mode of transport concerned.

Like the DOT regulations, both regulatory standards are based on the UN Recommendations, so their provisions are fundamentally consistent with those in the DOT regulations. For the general requirements that apply to the transport of lithium ion batteries under these standards, the same general philosophy would apply equally. However, since questions could be raised by international transport authorities regarding the direct applicability of those standards to the international transport of lithium ion batteries, confirmation by the appropriate international regulatory authorities of the applicable requirements is advisable.

To the extent that the foregoing analysis suggests the need for certain changes or clarifications to the applicable DOT regulations, corresponding changes to the international requirements would be equally appropriate. No procedure exists under these standards to obtain exemptions except by obtaining authorization from each country through which a shipment may pass. As a result, an exemption for international transport is generally neither desirable nor practical. To the extent the foregoing discussion of the domestic transport requirements suggests obtaining regulatory relief by seeking a DOT exemption, a similar approach may not be workable on an international level. Providing the necessary relief and clarification by amending the relevant regulatory standards is preferable.

Conclusions

Because the lithium ion battery is a developing technology that may employ different chemistries and different design characteristics (e.g., some may feature a design in which the electrolyte is "starved," whereas others may not), lithium ion batteries may pose a wide range of hazards in transport. In addition, the state of a battery's charge and whether it has been cycled (i.e., whether the carbon electrode has been lithiated), are important factors in determining the hazard posed by a lithium ion battery and, consequently, the regulatory requirements that apply to its transport. Therefore, lithium ion batteries may be subject to widely varying transport requirements—or may even be considered nonhazardous for transport and not subject to regulation—depending on the characteristics of a particular battery.

Many factors that affect the regulatory requirements applicable to transporting a lithium ion battery may, at least to some degree, be within the manufacturer's control. The manufacturer may have some ability to choose the level of regulation to which its battery may be subjected, and limit or control distribution costs and complexities. For example, a manufacturer may choose to ship newly manufactured batteries before applying an initial charge so the batteries may qualify as nonhazardous and be fully unregulated in transport. The manufacturer may also have flexibility to use a "starved" electrolyte system, or select electrolyte solvents with flashpoints sufficiently high to be above the regulated range. Factors that may affect the level of regulation that will apply to lithium ion battery transport must be considered at an early stage in battery design and development in an effort, where practicable, to implement design options that will minimize the level of regulation to which a particular design will be subject. Notwithstanding the possibilities to transport certain uncycled lithium ion batteries under a minimal level of regulation, or perhaps even as unregulated, transport of cycled batteries in various states of charge will inevitably be necessary and will be subject to regulation. The existing regulations for transporting lithium batteries were based on ensuring the safe transport of batteries and cells containing lithium metal or alloy. Thus, the suitability of these requirements for the transport of lithium ion batteries is uncertain. Of particular concern is that applying the existing lithium battery provisions to the transport of cycled, charged lithium ion batteries may subject these batteries to a regulatory regime that is unnecessarily onerous and restrictive. This results in unwarranted compliance and shipping costs and can lead to numerous practical problems in transport and distribution. If lithium ion batteries pose a significantly reduced level, or a different type of hazard in transport compared to batteries containing lithium metal, transport regulatory agencies should be requested to establish specific and unique transport requirements for lithium ion batteries that take into account the relative safety of these batteries in transport.

Before the regulatory agencies can be approached to develop and implement specific regulations to govern the transport of lithium ion batteries, those authorities must be satisfied that lithium ion batteries pose a significantly reduced level, or distinctly different type, of hazard in transport compared to batteries that contain lithium metal. To support this contention, certain information regarding the possible transport hazards posed by lithium ion batteries would have to be made available. This information would include:

1. Results of tests, performed in accordance with the Division 4.3 classification procedures, indicating the rate at which the lithiated carbon electrode (in various states of charge) evolves flammable gas on contact with water

2. Any other information that demonstrates differences in the inherent hazards posed by lithium ion batteries compared to batteries that contain lithium metal.

This information should be developed as soon as possible to determine whether a case can be made for the development of unique transport requirements for cycled, charged lithium ion batteries, or whether such batteries should be transported under the existing requirements applicable to lithium batteries. Research consistent with this recommendation is anticipated. If transport under the existing requirements were indicated, specific regulatory agency approvals might be required to allow the transport of batteries and cells of the size that would be used in EV applications. If, on the other hand, unique lithium ion battery transport requirements are to be developed, efforts in this connection should be commenced as soon as possible so that provisions will have been established by the time large-scale transport of lithium ion batteries for EV applications is expected to take place.

Summary

Lithium ion batteries are considered a mid- to long-term candidate technology for EVs. Lithium systems can achieve higher energy density than cells and batteries based on other elements. The lithium ion system has better reliability and reduced reactivity compared to present lithium metal batteries, and may have performance advantages compared to some lithium solid polymer electrolyte batteries. Thus, lithium ion technology is the focus of much commercial interest. Evaluation of EH&S issues of the lithium ion technology is an essential part of the development and commercialization of lithium ion batteries for EVs. This report has provided an initial EH&S assessment.

This report has considered cell chemistry, materials selection, intrinsic material hazards, mitigation of those hazards, environmental requirements, pollution control options, and shipping requirements for lithium ion EV batteries. Many of these issues cannot be definitively presented at this time, because the technology is still under development. Materials for lithium ion EV batteries may change, and with them, the health and safety hazards, environmental concerns, and shipping requirements. Despite these uncertainties, this report has considered materials that seem likely to be used in lithium ion EV batteries.

Health and safety hazards, such as toxicity, carcinogenicity, and reactivity, are intrinsic to some lithium ion battery materials, although battery design and workplace practices can mitigate such hazards. Toxic materials include lithium compounds, nickel compounds, arsenic compounds, fluorides, and DME; carcinogenic materials include nickel compounds and arsenic compounds; lithiated negative electrode materials could be reactive. Some possible battery materials, especially lithium and arsenic, would be subject to environmental regulations during recycling or disposal. Shipping requirements will depend, in part, on the reactivity of the negative electrode materials and the flammability of the organic liquid electrolyte. Thus, EH&S issues will be fundamental considerations in the commercialization process.

Designing cells and batteries to achieve adequate performance is likely to mitigate many material hazards, as engineering design for reliability and durability will also enhance safety. Design attributes can mitigate material hazards by containing the battery materials and reducing the chance of a hazardous chemical reaction. Thermal management of the battery system, electrical protection, containment of battery materials, and venting of gases can reduce the hazards of a lithium ion system. Workplace practices can mitigate occupational hazards. However, safety testing of EV-sized batteries will be needed.

Environmental laws and regulations at the local, state, and federal levels will apply to air emissions, water effluents, and land disposal of lithium ion battery wastes. This report outlined the relevant parts of CWA, CAAA, and RCRA.

Waste minimization addresses the environmental regulation of possible battery materials. It can reduce the environmental impacts, and the burden of environmental compliance, of lithium ion battery manufacturing. Possible recovery and recycling techniques for some battery materials have been described, including recovery of metals and recycling of plastics. These techniques may warrant further research and development as the volume of spent batteries increases.

Lithium ion batteries that are "dry," and do not pose other hazards in transport, are not subject to hazardous material transportation regulations. Several factors determine shipping requirements: whether the battery has been cycled; how electrochemically active it is; and whether it has free electrolyte. Manufacturers may be able to select battery designs with relatively few shipping requirements. However, new lithium ion battery shipping regulations may be advantageous if shipping hazards of lithium ion batteries can be shown to differ significantly from batteries containing lithium metal, upon which existing regulations are based. Research on the shipping hazards of lithium ion batteries is anticipated.

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13. ABSTRACT *(Maximum 200 words)*

Lithium ion batteries are mid- to long-term candidates for propelling electric vehicles. In theory, lithium-based batteries can achieve a higher energy density than systems using other elements. In addition, the lithium ion system is less reactive and more reliable than present lithium metal systems and has possible performance advantages over some lithium solid polymer electrolyte batteries. Understanding the environmental, health, and safety issues associated with these batteries is an important step toward their commercialization. Analysts at the National Renewable Energy Laboratory studied these issues, and their findings are presented in this report. They reviewed a system that uses lithium intercalation compounds for the positive and negative electrodes and an organic liquid and a lithium salt for the electrolyte. The study considered cell chemistry, materials selection, intrinsic material hazards, mitigation of those hazards, environmental requirements, pollution control options, and shipping requirements. Some possible lithium ion battery materials were found to be toxic or carcinogenic. The report recommends further research on the hazards of possible chemical reactions in lithium ion batteries. However, the report states that cells and batteries designed to be reliable and durable will likely mitigate material hazards as well. Analysts suggest that minimizing waste during manufacturing and at the end of the battery life could reduce the burden of environmental compliance. In addition, they discuss various regulatory options for shipping lithium ion batteries.

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