6. Battery Hazards and Safety

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OUTLINE

- Key hazards batteries are exposed to and key hazards batteries produce
- Electrochemical vs. chemical energy release
- Thermal propagation
- High voltage hazards
- Test and characterization methods
- Mitigation and control strategies
### THE HAZARDS FOR BATTERIES AND EVs

- A battery is an active energy storage device:
  - Its operation to perform its primary function gets it de-energized: lack of control of such an operation creates hazards.
  - It is unlike a fuel tank, which can be drained of fuel passively without the operation of the device.
- A key battery function is to isolate the electrochemical components from the environment and vice versa; the failure of this function leads to many of the hazards we associate with batteries.

### REVIEW OF THE EV BATTERY PRIMARY FUNCTIONS

- Provide electrical power
- Accept electrical power
- Control state of function
- Communicate with the host (vehicle)
- Store electrochemical energy

![Diagram of an electric vehicle with battery and electric motor drive unit]
THE FUNCTION – HAZARD LOOP

- External hazards can lead to functional failures
- Functional failures can lead to internal hazards
- Internal hazards can propagate to become external hazards

LIST: HAZARDS RELATED TO EV BATTERIES

- Most hazards can be captured within this list:

<table>
<thead>
<tr>
<th>external hazards</th>
<th>internal hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>debris impact to enclosure</td>
<td>isolation failure</td>
</tr>
<tr>
<td>excessive heat / fire</td>
<td>internal short circuit</td>
</tr>
<tr>
<td>water immersion</td>
<td>excessive cell temperature</td>
</tr>
<tr>
<td>static load</td>
<td>vented gas products</td>
</tr>
<tr>
<td>external electrical short</td>
<td>fluid leak</td>
</tr>
</tbody>
</table>
**Li-ION TECHNOLOGY**

- Today’s predominant battery technology
- Highest rechargeable battery energy density (Wh/l) and specific energy (Wh/kg)
- Excellent cycle life and durability
- High-cell voltage (e.g., 3.6 V) implies aqueous electrolytes cannot be used and organic solvent-based electrolytes are used instead
- Flammability concerns – particularly, when coupled with the high material energies
**TABLE OF COMMON ELECTROLYTE MATERIALS**

Batteries currently use $\text{LiPF}_6$ (lithium hexafluorophosphate) salt in organic solution of ethylene carbonate (EC) solvent and other viscosity modifiers (diethylcarbonate (DEC), dimethylcarbonate (DMC), ethylmethylcarbonate (EMC)): for example is 1.2 M $\text{LiPF}_6$ in 3:7 EC:EMC – is considered a standard test electrolyte.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene carbonate (EC)</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>Vinyl ethylene carbonate (VEC)</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>Lithium hexafluorophosphate</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>Dimethyl carbonate (DMC)</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>Ethyl methyl carbonate (EMC)</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>Diethyl carbonate (DEC)</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
</tbody>
</table>

**ELECTROLYTE MATERIALS**

- The EC is a solid at room temperature and dissolves the salt and provides the ionic transport for both the $\text{Li}^+$ cations and the $\text{PF}_6^-$ anions.
- The other carbonates dissolve and dilute the EC to lower the electrolyte viscosity and make it more volatile.
- Plays a large role in the development of stable SEI – solid electrolyte interphase – to allow passage of Li- ions and prevent surface electrolytic reduction.
SOLID ELECTROLYTE INTERPHASE (SEI) LAYER

- **SEI** layer forms on the anode (carbon) surfaces
- Ionically conductive, electronically insulative layer
- Created during *initial charge* in the formation process
  - reduction of electrolyte solution onto the carbon surface
  - main organic carbonate (*EC* or *PC*) react with Li to form soluble Li-oxide within organic structure

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ELECTROLYTE ISSUES

- **LiPF₆** is sensitive to water, decomposing to form hydrofluoric acid (**HF**) and fluoro-phosphoric acid
- High temperatures (> 55°C) will also encourage decomposition of the salt under the voltages seen within the cell
  - the acids attack the anode and cathode, leading to the destruction of the cell
  - stabilizers are added to electrolyte to mitigate these issues
ELECTROLYTE ISSUES

- LiPF₆ also decomposes at potentials around 4.5 V
- Other salts are being considered as well (LiTFSI and other Imides, “LiBOB”, LiBF₄)
- Solvent flammability/volatility

Common Electrolyte Salt

- LiPF₆ - Li hexafluorophosphate - this salt is almost exclusively used in current Li-ion batteries because it provides the best mix of the required properties; con - easily reacts with water to form HF
- LiAsF₆ - Li hexafluoroarsenate - similar performance to Li hexafluorophosphate without HF formation; con - arsenic is highly toxic
- LiClO₄ - Li perchlorate – one of the first salts studied, but abandoned due to explosivity
- LiFSI and LiTFSI - “imide salts” – these salts are under intensive research currently for use with the next generation materials (silicon, 5 V cathodes) due to the high thermal stability and stability with water

CHEMICAL vs. ELECTROCHEMICAL ENERGY

- Graphite + Li:
  \[ C_6 + Li = LiC_6; \ 4.9 \text{ kJ/g} \]
  \[ LiC_6 + 6\ 1/4 \ O_2 = \frac{1}{2} \ Li_2O + 6 \ CO_2; \ 63.6 \text{ kJ/g} \]
- In the presence of oxygen and heat, the energy per gram of lithiated graphite anode released is 13 X that of the stored electrochemical energy
- A similar issue is faced by the decomposition of a metal oxide anode
CATHODE ELECTROCHEMICAL DECOMPOSITION

- A classic metal oxide cathode material has this formulation:
  \[ \text{LiMO}_2; \ M=3^+ \]
- However, when charged the amount of lithium is considerably less:
  \[ \text{Li}_{1-x}\text{MO}_2; \ M = (1 - x) \ 3^+ \& \ x4^+ \]
- The cathode is prone to decompose to more table materials, under heat, releasing heat and oxygen:
  \[ \text{Li}_{1-x}\text{MO}_2 \rightarrow (1-x)\text{LiMO}_2 + x\text{O}_2 \ ; \ M = 3^+ \]

Remember: the anode reaction and the fuel triangle!

DISTRIBUTION OF EV/PHEV FIRES

95 vehicle types:
make / model / year
CELL POWER & HEAT GENERATION

**cell specifications:**
- capability ($C$): 25 Ah
- nominal DC resistance ($R$): 0.5 mohm
- $V_{\text{max}}$: 4.2 V
- $V_{\text{nom}}$: 3.68 V
- specific heat capacity ($Q_h$): 1 kJ/kg K
- specific energy: 250 Wh/kg

**key equations:**
- power ($P$) = $V_{\text{min}} \cdot (V_{\text{max}} - V_{\text{min}}) / R$ (W)
- current ($I$) = $P / V_{\text{min}}$ (A)
- $P_{\text{heat}} = I^2 \cdot R$ (W)
- $Q_{\text{heat}} = P_{\text{heat}} \cdot t$ (J)

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CELL UNDER UNCONSTRAINED DISCHARGE

Based on the cell specifications given in the previous slide

[Graph showing power, current, and heat generation vs. voltage under discharge load]
Assumptions: adiabatic condition and the current can be maintained throughout the discharge

The temperature rise looks incredible!

Assume a 10-s discharge at a specified voltage $V_{max}$:

<table>
<thead>
<tr>
<th>10s discharge</th>
<th>$V_{min}=f(V_{max})$</th>
<th>I (A)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2V_{max}/3$</td>
<td>3 V</td>
<td>933</td>
<td>36</td>
</tr>
<tr>
<td>$V_{max}/2$</td>
<td>2 V</td>
<td>1400</td>
<td>80</td>
</tr>
<tr>
<td>$V_{max}/3$</td>
<td>1 V</td>
<td>1867</td>
<td>142</td>
</tr>
<tr>
<td>$V_{max}/4$</td>
<td>1 V</td>
<td>2100</td>
<td>180</td>
</tr>
</tbody>
</table>

Assume cell is adiabatic, even though there will be heat rejected into the environment.

The table shows the potential temperature rise that can be achieved inside the cell.
THERMAL RUNAWAY ISSUES

- An issue for ALL Batteries.
- Of particular interest for Li-ion, due to high energy density AND the use of flammable electrolytes
- Both cathode and anode materials will exothermically decompose, at elevated temperatures.
- The energy levels are exacerbated with higher state of charge (s.o.c.)

![Graph showing temperature over time for different battery materials]

THE 3 STAGES OF CELL THERMAL RUNAWAY

Source: K. Liu, Y. Liu, D. Lin, A Pei, Y Cui; Materials for Li-Ion Battery Safety, http://advances.sciencemag.org/June 22, 2018
SOME SALIENT Li-ION CELL TEMPERATURES

Some temperature-based events:

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>-46</td>
<td>Most electrolytes precipitate salt or freeze</td>
</tr>
<tr>
<td>-40 to +55</td>
<td>Operating range</td>
</tr>
<tr>
<td>+65</td>
<td>Electrolyte salt instability against graphite</td>
</tr>
<tr>
<td>+85</td>
<td>SEI layer begins to dissolve, allowing electrolyte reaction with anode</td>
</tr>
<tr>
<td>+115</td>
<td>Earliest onset of metal-oxide cathode decomposition</td>
</tr>
<tr>
<td>+130</td>
<td>Melting Point of Polyethylene (separator)</td>
</tr>
<tr>
<td>+140</td>
<td>Flashpoint of some electrolyte solvents</td>
</tr>
<tr>
<td>+150</td>
<td>Melting Point of Polypropylene (separator)</td>
</tr>
<tr>
<td>+180</td>
<td>Melting Point of Li metal</td>
</tr>
<tr>
<td>+210</td>
<td>Metal Phosphate Decomposition</td>
</tr>
<tr>
<td>+680</td>
<td>Melting Point of Al metal</td>
</tr>
</tbody>
</table>

MORE ON CELL PROPAGATION

GTR No.20 proposes notification of thermal event to occupant and provides at least 5 minutes to egress vehicle, before propagation between cells leads to enclosure breach.
VOLTAGE RANGES

- A single cell is, typically, operating between 2.8 V and 4.2 V, with 3.7 V nominal value.
- Cells are connected in series, in order to deliver more power.
  - EVs will often have ~100 cells in series – 400 V systems
  - More recent systems have around 200 cells in series – 800 V systems

ELECTRIC SHOCK

Electric Shock

- Electrical current passing through the human body can cause:
  - Cardiac arrhythmia (heart beats irregularly) or cardiac arrest (heart stops beating)
  - Skin and tissue burns
  - Nerve damage
  - Amputation
  - Blindness
  - Possible death

It takes as little as 100 mA of direct current to induce cardiac arrhythmia.
This can be achieved with as little as 60 V across dry skin.
DEFINITION OF HIGH VOLTAGE

**EVs** have hundreds of volts in their propulsion system, providing opportunity for arc flashes.

An arc flash can cause blindness, severe burns and tissue damage.
TYPICAL *HV*-RELATED *EV* LABELS

- Lithium-Ion Battery Warning Labels
- First Responder Label
- First Responder Cable Cut Label
- Shock Warning Label

THE PARTS OF AN *HV* PROPULSION SYSTEM

- HVIL circuit
- High Voltage Connectors
- Battery Pack Internal Cables
- High Voltage Wiring
- Power Inverter Module (PIM)
- High Voltage Wiring
TWO–POINT ISOLATION / ONE–POINT TOUCH

- two-point isolation:
  - -ve isolated from enclosure
  - +ve isolated from enclosure

- potential but no return path

- 500 $\Omega/V$
- 1,000 $V_{DC}$

design min

most HV batteries continuously monitor electrical isolation between each leg and the enclosure

THE BATTERY HV SYSTEM
## HIGH VOLTAGE INTER – LOCK (HVIL)

- A low voltage (5-12 V) circuit within the battery and other HV components within the propulsion system, routing through all HV connections and access panels (through which HV can be accessed)
- Often sourced by the battery manufacturer as part of the Battery Management System
- The signal is normally a pulse wave modulated (PWM) signal, under 10 mA
- The return of the signal is sensed within the battery and at least at one additional point in the propulsion system
- Loss of the signal indicates attempted access to HV, allowing effective response, i.e., battery command contactors open

### TEST AND CHARACTERIZATION METHODS

- Batteries can be tested for their behavior under, and response to, abusive conditions
- Conditions can be electrical, mechanical, thermal, environmental or functional
- Many standardized test methods exist; test choice usually depends, typically, on the purpose of the specific characteristic investigated
**ELECTRICAL ISSUES**

- External short circuit – a sustained electrical discharge, usually targeting the same resistance as the cell, but often at varying levels.
- Over-charge – charging a cell to a voltage and capacity above 100% s.o.c. setpoint; tests vary but a common characterization test – USABC – charges the device to 200% rated capacity, limited to 125% maximum voltage.
- Over-discharge – discharging a cell into reversal, by attempting to remove from full charge 200% of its rated energy capacity.

**MECHANICAL TESTS**

- Overall tests seek to either induce an internal electrical short or a mechanical failure.
- Crush – deform a device along each of its axes.
- Shock – provide an impulse to the device under each of its major axes.
- Vibration – similar to a shock, but signal is smaller amplitude and varied over a frequency range.
- Drop/impact – drop device onto a surface or impact the device with a projectile.
- Penetration – drive a penetrating object into the device.
THERMAL/ENVIRONMENTAL FEATURES

- Heating – raise the temperature of the device and determine the onset point of thermal runaway and characterize the observed results
- Thermal Shock – repeatedly expose device to alternate thermal extremes
- Water Immersion – submerge the device in water – usually saline
- Humidity – expose device to higher temperatures and non-condensing humidity

FUNCTIONAL TESTS

- Verify the device’s response to all-type hazards
- Thermal – isolation of battery from host under extreme thermal conditions
- Electrical – verification that the active and passive devices correctly intervene operation on overcurrent, over-voltage and under-voltage
- Mechanical – monitor primary and secondary effects, and intervene on function
BATTERY & ENVIRONMENT: HAZARD & RISK (OPERATIONAL SAFETY) EXAMPLES

- **-safe operating zone**
- **limited operation**
- **Hazard**

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**cell (NMC/C):**

- 4.35 V'
- 4.25 V'
- 2.80 V'
- 2.10 V'

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RISK EVALUATION

- **Severity of possible accident**
  - incident
  - Not acceptable
  - Tolerable Risk
  - Acceptable

- **Frequency**
  - always
  - remote
  - negligible
  - lower than tolerable risk

- **Safety class (ASIL):**
  - Required ASIL, e.g., failure rate of safety function
  - ASIL: Automotive Safety Integrity Level

- **Tolerable Residual Risk**

- **Severity**
  - catastrophic
  - negligible

- **Probability of Exposure to driving situation**
  - Risk reduction due to external measures e.g., controllability by the driver

**Functional safety related to control systems, their algorithms and software. Please refer to ISO26262**
TYPICAL FUNCTIONAL SAFETY REQUIREMENTS FOR 48-V Li-ion BATTERY

<table>
<thead>
<tr>
<th>Item</th>
<th>ID</th>
<th>Hazard</th>
<th>ASIL</th>
<th>Safety Goal</th>
<th>Safe State</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMS</td>
<td>1</td>
<td>The specified maximum cell voltage limit is exceeded without safe reaction.</td>
<td>C</td>
<td>Maximum cell voltage violation shall lead to the safe state.</td>
<td>Contactor open</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>The specified maximum cell temperature limit is exceeded without safe reaction.</td>
<td>C</td>
<td>Maximum cell temperature violation shall lead to the safe state.</td>
<td>Contactor open</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>The specified maximum cell current limit is exceeded without safe reaction.</td>
<td>C</td>
<td>Maximum battery current violation shall lead to the safe state.</td>
<td>Contactor open</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>The specified minimum cell voltage limit is exceeded without safe reaction.</td>
<td>C</td>
<td>Every minimum cell voltage violation shall lead to the safe state.</td>
<td>Contactor open</td>
</tr>
</tbody>
</table>

Similar efforts are applied to the powertrain controller.

PROPAGATION MITIGATION STRATEGIES

- Controls: prevent operations that leads to cascading failures
- Electrochemistry: construct thermally stable solutions via deployment of active materials/electrolytes
- Mechanical design: direct energy release/venting
- Thermal design: insulate between cells and within pack; in the future, introduce immersion
VENT GAS MANAGEMENT

- A Li-ion cell can produce ~ 5 l gas/Ah in the process of complete decomposition; a cell, typically, produces about half this volume.
- Gas must be managed within the battery and off-board of the vehicle.
- Gas pressure, gas flow and gas temperature management through proper routing.

HIGH CURRENT MANAGEMENT

- Contactors rated to voltage and peak current.
- Thermal fuses.
- “Smart” fuses/pyrofuses/breaker-style switches.
- Redundant current measurement.

Example: current vs. time plot for a thermal fuse.