U.S. Department of Transportation

Pipeline and Hazardous Materials Safety Administration

Welcome to the

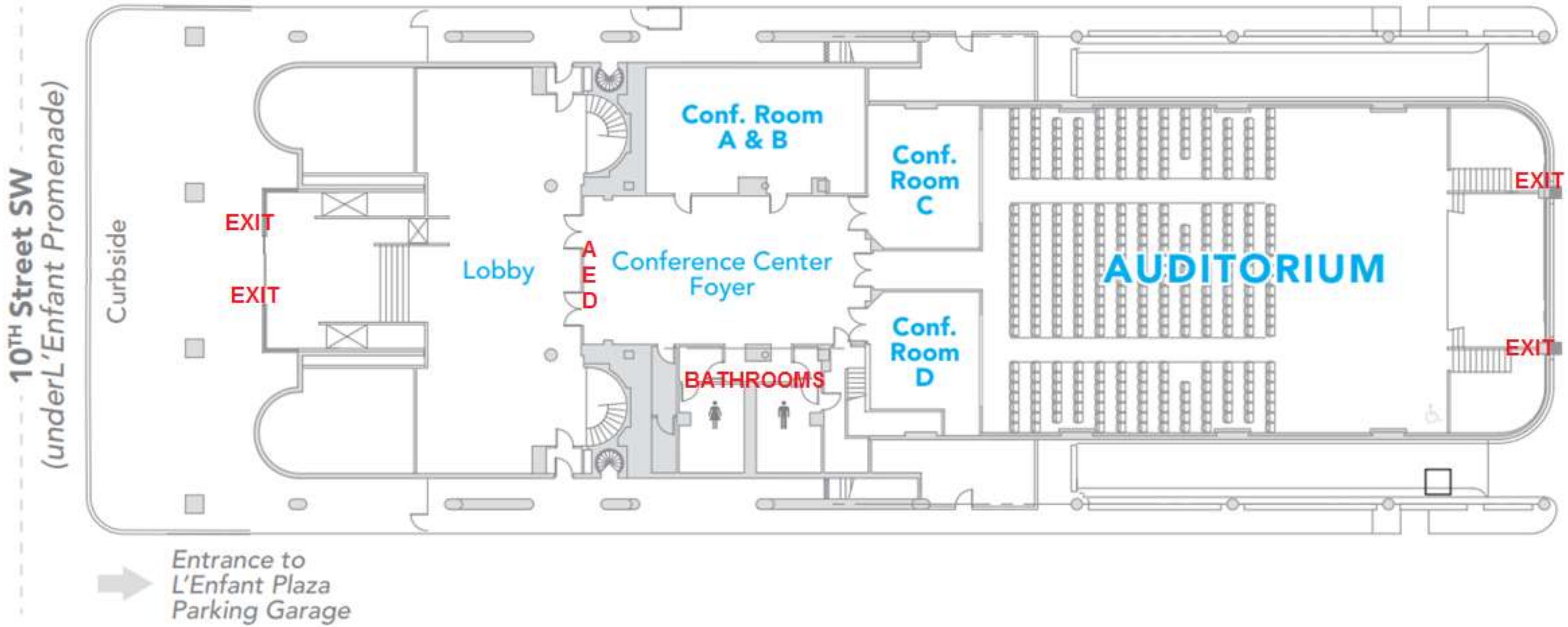
U.S. Department of Transportation's

Office of Hazardous Materials Safety

Research & Development Forum

National Transportation Safety Board

420 10th Street SW, Washington DC 20594



U.S. Department
of Transportation
Pipeline and
Hazardous Materials
Safety Administration

Have a Question?
Email: hazmatresearch@dot

U.S. Department of Transportation

Pipeline and Hazardous Materials Safety Administration

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Research & Development Forum

Research and Development
Office of Hazardous Materials Safety

Rick Boyle

Office of Hazardous Materials Safety
Research and Development Program

May 16, 2018

Overview

Introduction

- Strategic Framework

Program Assessment

- Strategic Planning
- Maturity Model

Research Overview

- 2017 BAA and Ongoing Projects
- 2018 Acquisition Planning

Mission Statement

To provide research, analyses and technical information needed to manage the public risk associated with hazardous material transportation; provide the analytical foundation for regulatory and outreach activities; enhance multi-modal enforcement initiatives; and provide alternative opportunities for training development.

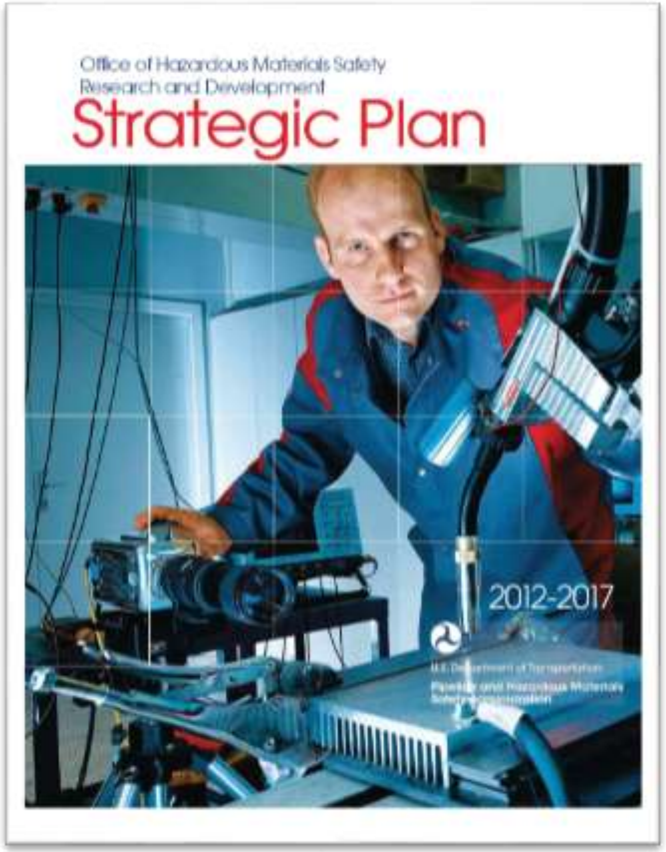
Strategic Goals

- Promote continuous safety improvement
- Invest in innovation
- Build greater public and stakeholder trust
- Cultivate organizational excellence and safety culture
- Pursue operational excellence in our processes and our data

Strategic Objectives/Actions

Strategic Goals	Strategic Objectives / Actions
Promote continuous safety improvement	BAA Strategic Areas of Risk Assessment and Management and Technical Analysis
Invest in innovation	BAA Strategic Areas of Emerging Technology and Packaging Integrity
Build greater public and stakeholder trust	R&D Forum and Public Meetings; Cooperative research; Gap Analyses and Research Needs Statements; Website Development
Cultivate organizational excellence and safety culture	Strategic Plan; Annual Modal Research Plan; SME and Contract Support
Pursue operational excellence in our processes and our data	Management Information System; SOP Development

Strategic Planning



VEDA'S NEW AND IMPROVED STRATEGIC PLAN

2018 - 2023

Maturity Model

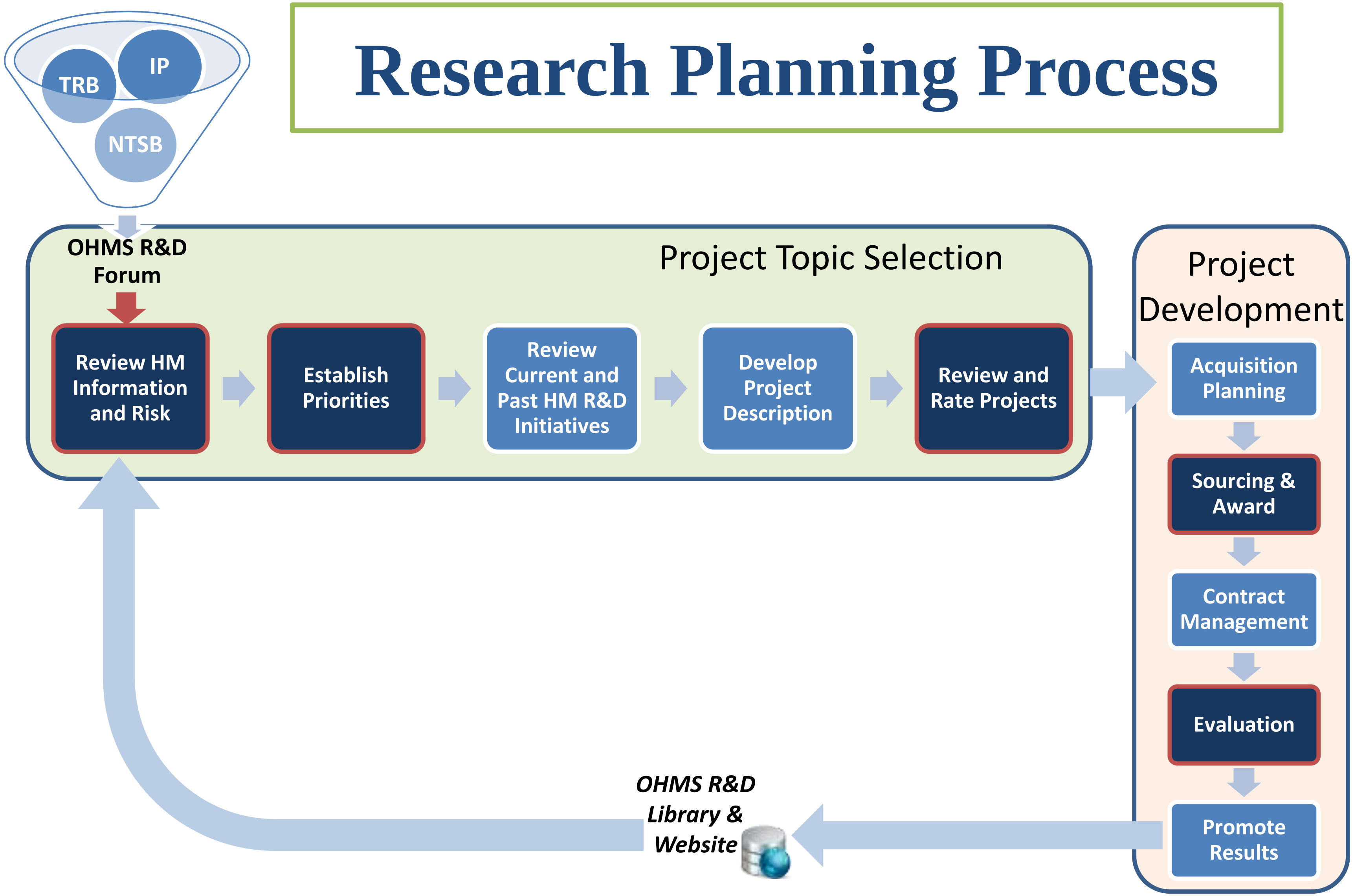
Maturity Level	Level 0: Absent	Level 1: Developing	Level 2: Functioning	Level 3: Integrated	Level 4: Optimizing
Organization	Informal, basic roles, responsibilities decentralized. Conceptual awareness.	Projects are sponsored, informal inventory of skills. Certain business drivers identified; tactical priorities set.	PMO established, roles and training needs are defined. Business-aligned vision defined; strategic priorities set.	PMO active, RACI matrix defined; proactive skill development. Vision and strategy continually reviewed to track business strategy.	Optimal integration with business skills optimized. Periodic optimization of vision and strategy.
Methods and Processes	Processes are unpredictable, poorly controlled, reactive.	Processes are planned, documented, performed, monitored, and controlled at the project level. Often reactive.	Processes are well characterized and understood. Processes, standards, procedures, tools, etc. are defined at the organizational level. Proactive.	Processes are controlled using statistical and other quantitative techniques.	Process performance continually improved through incremental and innovative technological improvements
Program Operations	Possible use of target-specific productivity tools	Disjointed projects; Disparate structure and localized efforts.	Discrete architecture defined	Architecture redefined and aligned with EA	Architecture embedded with EA; optimization

2017 Broad Agency Announcement

Eva Rodezno

In 30 Minutes !

Research Planning Process



2018 Acquisition Planning

- Improve Scheduling/Incorporate Lessons Learned
- Expand/Refine Strategic Topic Areas
  - 2017 BAA Submissions; Modal Partner Programs
  - New Strategic Plan; New Forum Input
  - New Administration; New Budget
- Revise Submission Requirements
  - Problem identification
  - Outcome/Product Identification
  - Broaden response candidates
- Improve Evaluation/Prioritization
  - Include SME
  - Additional Assessment Criteria

Questions?

Rick Boyle

Office of Hazardous Materials Safety
Research and Development Program

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HM-10(1): Current Hazardous Materials Transportation Research and Future Needs, Phase 2

PHMSA OHMS 2018 R&D Forum

May 16th 2018

FACTOR

Overview

- Project Scope
- Relevant Research Organizations
- Perceived Research Gap Areas
- Research Prioritization Framework
- Prioritized Projects
- Questions

Project Scope

- Identify organizations conducting or sponsoring hazmat transportation-related research
- Identify recent, ongoing, and planned hazmat transportation-related research
- Organize by context and subject areas
- Identify future research needs
- Document gaps and overlaps and suggest research projects to fill the gaps
- Develop prioritization framework
- Prioritize the research projects

Relevant Research Organizations (1 of 3)

FEDERAL - DEPARTMENT OF ENERGY	# Projects
Department of Energy	2
Oak Ridge National Laboratory (ORNL) Center for Transportation Analysis (CTA)	2
Savannah River National Laboratory (SRNL)	3
FEDERAL - DEPARTMENT OF HOMELAND SECURITY	
Federal Emergency Management Agency (FEMA)	7
Transportation Security Administration (TSA)	2
FEDERAL - DEPARTMENT OF TRANSPORTATION	
Federal Aviation Administration (FAA)	2
Bureau of Transportation Statistics (BTS), Office of Survey Programs	1
Federal Motor Carrier Safety Administration (FMCSA)	13
Federal Railroad Administration (FRA)	21
Maritime Administration (MARAD)	1
Pipeline and Hazardous Materials Safety Administration (PHMSA) Office of Hazardous Materials Safety (OHMS)	51
Pipeline and Hazardous Materials Safety Administration (PHMSA) Office of Pipeline Safety (OPS)	139
US Transportation Command (USTRANSCOM)	1
FEDERAL - ENVIRONMENTAL PROTECTION AGENCY	
Environmental Protection Agency Office of Emergency Management (EPA OEM)	3

Relevant Research Organizations

INTERNATIONAL	# Projects
Transport Dangerous Goods Directorate (TDGD)	17
STATES	
California Office of Emergency Services (CalOES)	2
Commercial Vehicle Safety Alliance (CVSA)	1
National Council of State Legislatures (NCSL)	1
INDUSTRY ASSOCIATIONS	
Cargo Tank Risk Management Committee (CTRMC)	9
SHIPPERS	
American Chemistry Council (ACC)	1
Chlorine Institute (CI)	4
E. I. du Pont de Nemours and Company (DuPont)	3
Institute of Makers of Explosives (IME)	9
CARRIERS	
American Transportation Research Institute (ATRI)	5
Association of American Railroads (AAR)	6
RESPONSE	
International Association of Fire Chiefs (IAFC)	2

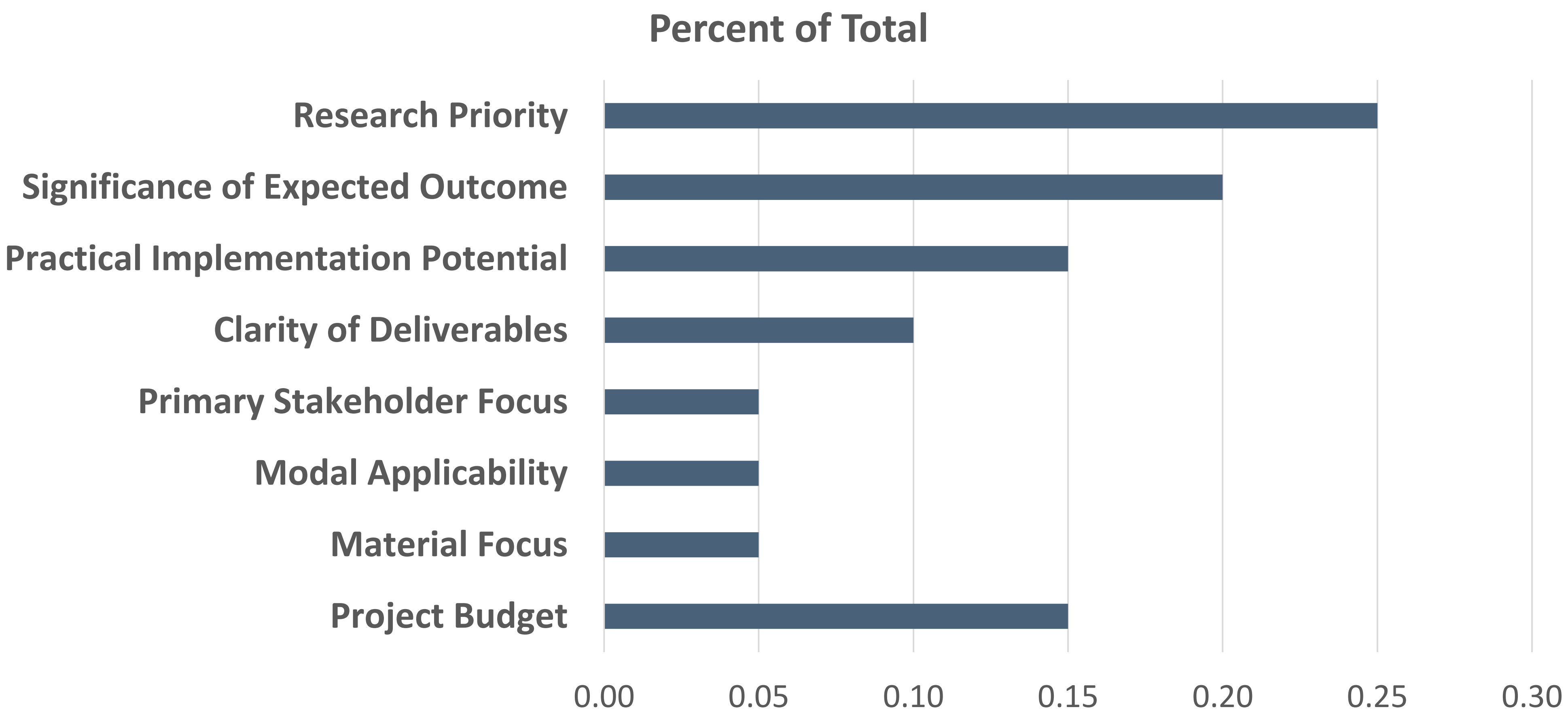
Relevant Research Organizations (3 of 3)

ACADEMIC/RESEARCH	# Projects
Johns Hopkins Applied Physics Laboratory (JHU APL)	4
Mary Kay O'Connor Process Safety Center, Texas A&M Engineering Experiment Station (PSC-TAMU)	5
McGill University	12
McMaster University	10
Texas A&M Transportation Institute (TTI/TAMU)	9
Transportation Research Board (TRB)	22
University of Illinois, Urbana Champaign, RailTEC	3
University of Kentucky/Kentucky Transportation Center (KTC)	1
Vanderbilt University	9
DHS UNIVERSITY CENTERS	
Maritime Security Center (MSC)	12
National Center for Risk and Economic Analysis of Terrorism Events (CREATE)	4
National Consortium for the Study of Terrorism and Responses to Terrorism (START)	4

Perceived Research Gap Areas

- **Cargo Packaging and Handling**
  - Safety and Reliability Features
  - Data Development and Safety Testing
- **Emergency Planning and Response**
  - Guidance Development
  - Education and Training
  - Communication, Tracking, and Detection
  - Planning and Commodity Flow Data
  - Equipment
- **Materials and Equipment Testing**
  - Hazardous Material Characterization and Testing
  - Package Lining and Corrosion Resistance
  - Standards
  - Monitoring and Inspection
- **Risk Analysis and Perception**
  - Hazards, Risks, and Mitigation
  - Data Development
  - Modeling Techniques
  - Systems Approaches
  - Risk Communication and Perception
  - Hazmat Release Consequences
- **Emerging Materials and Technologies**
  - Batteries and Emerging Energy Products
  - Automated and Connected Vehicles
  - Technologies for Safety and Decision Making
- **Operations and Infrastructure**
- **Regulatory or Economic Considerations**
- **Training and Education**

Research Prioritization Framework



Prioritized Projects (1 of 3)

Proposed Project	Rank		
	Excl. Cost	Incl. Cost	Using B/C
Use of Technology to Facilitate Multiple Stakeholder Communications and Information Exchange, Emergency Response Deployment, Decision-Making, and Community Emergency Response Preparedness	1	7	11
Best Practices for LNG Incident Response	2	1	1
Understanding Failure Rates of New and Reconditioned Hazmat Drums in Transportation	3	3	4
Understanding Impact of Recycled Material Content on Failure Rates of Hazmat Containers	3	3	4
Best Practices for Large Storage Battery Incident Response	3	2	3
Advanced Technical Capabilities for Evaluation of Infrastructure Condition	6	5	6
Reducing Fall and Confined-Space Entry Risks to Workers through Technology Employed at Ground Level	7	9	10
Identification of Potential Improvements to the Emergency Response Guidebook's Guidelines for Chlorine Incident Protective Distances	8	6	2
Understanding and Preparing for Changes in Lithium Battery Uses, Characteristics, and Commercial and Non-Commercial Transportation	8	7	7
Methodology and Criteria for Vibration Testing of Hazmat Packages Under Conditions Representative of All Modes of Their Transport	10	11	12
Understanding the Performance of Plastic Composite Intermediate Bulk Containers (IBCs) Under Conditions Representative of All Modes of Their Transport	11	10	8

Prioritized Projects (2 of 3)

Proposed Project	Rank		
	Excl. Cost	Incl. Cost	Using B/C
Methodology and Criteria for Service Life Guidelines for Bulk and Non-Bulk Hazmat Packages	12	11	9
Identifying Sources and Types of Undeclared Hazmat and Associated Mitigation Strategies	13	13	13
Improved Methods to Assess Cost-Effectiveness of Various Rail Risk Mitigation Strategies to Realize Maximum Return on Investment	14	14	15
Identification of New Steels or Steel Properties for Tank Car Construction to Enhance Puncture Resistance	15	25	24
Development of an Overarching Structure for Assessing and Managing Risks through the Hazmat Transportation Supply Chain	15	22	21
Guidance on Reporting and Investigation of Road Accident and Hazmat Incidents for States, including Training Recommendations	17	15	14
Evaluation of the Effectiveness of Current Emergency Response Training Methods and Identification of Improvement Opportunities in Development and Delivery	18	17	18
Expansion of the Emergency Response Guidebook to Include Guidelines for Additional Materials	19	16	17
Advances in the Automatic Detection of Leaks in Transport Equipment	20	29	29

Prioritized Projects (3 of 3)

Proposed Project	Rank		
	Excl. Cost	Incl. Cost	Using B/C
Exploration of Advances in Self-Sealing Technology and Materials to Reduce Consequences of Transportation Equipment Breaches	21	23	25
Testing Methods and Criteria for the Classification of a Material as a Corrosive Solid	21	20	20
New Materials Research on Transportation Equipment Coatings and Linings	23	25	28
Improvements in Methods to Test and Classify Hazmat	23	30	30
Understanding the Potential Uses, Risks, and Risk Mitigation for Hazmat Transportation by Autonomous Vehicle	23	19	19
Understanding the Risks Associated with Unit Train Transport of Chlorine, LPG, and Other Materials	26	18	16
Methods for Improving Acquisition and Use of Hazmat Commodity Flow Data	27	21	22
Improved Guidelines for Classifying and Packaging High Net Explosive Weight Commodities (such as Munitions) for Transportation	28	23	23
Improved Understanding of Anhydrous Ammonia Release Behavior through Large-Scale Release Testing	29	31	31
Understanding the Risks Associated with Transport of Anhydrous Ammonia and Other Agri-Business Chemicals and Associated Mitigation Strategies	29	27	26
Estimating Consequences from Multiple-Material Releases in Transportation Incidents	29	27	26

U.S. Department of Transportation

Pipeline and Hazardous Materials Safety Administration

BREAK

Strategic Planning for OHMS Research & Development Program

Veda Bharath, PhD
Physical Scientist, R&D Branch
Engineering and Research Division

Outline

- Strategic outline
- Current state of program
- Strength-Weakness-Opportunity-Threats (SWOT) analysis
- Summary and next steps

Strategic Building Blocks

Outward/public facing strategic document

Concrete present objective that defines office existence

Clear statement that reflects the future aspiration of the program

Focused set of long-term, clear, specific outcomes the program will pursue to achieve vision

Set of strategic outcomes that describes what the program will do to achieve strategic goals

Each performance goal has a performance measure with measurable target and time (1/goal)

Planned programs, initiatives, interventions to achieve perform goals

Internal yearly-iterative performance plan

R&D Program – Current State

R&D progress:

- All R&D project management and research interaction is captured in a single system
    - Share point based MIS
- Standard Operating Procedures (SOPs) established to provide program framework and execution
- Defining program and project evaluation criteria
- Addition of staff (FTEs) for key roles in the program
- Planning documents and program accomplishments
- Obligate funds
    - Larger project base for execution (BAA)
    - Alternative spend mechanisms:
        - Innovation centers/Technology Accelerators
        - Joint R&D multi-year projects
- Gather input and feedback from all sources (process options)

R&D Program Areas

Current OHMS Program Areas

- Package Integrity
- Human Factors
- Technical Analysis to Aid Risk Assessments
- Risk Management and Mitigation
- Emerging Technologies

Proposed OHMS Program Areas

- Package Integrity
- Technical Analysis to Aid Risk Assessments (human factors)
- Risk Management and Mitigation
- Emerging Technologies

BAA

Research Project Emphasis

Staff Development Focus

OHMS R&D Program Areas are based on PHMSA Program Areas

S

Strengths

- Moderate budget
- **Strong technical expertise**
- **Good relationship with stakeholders, intermodal partners, other government agencies**
- Continued international partnerships
- Robust support functions: contracting and finance
- **Good status of current efforts: BAAs, seminar series, R&D forum**

W

Weaknesses

- **Low Contract Officer Representative (COR) ratio**
- Slow contracting time for some types of contracts
- **Insufficient resources to promote and expand the R&D program (outreach)**
- **Low institutional understanding of R&D, succession planning**
- **Missing functions, e.g., advisory board**
- Few opportunities for R&D specific training
- Clear bounds for R&D relative to other modes

O

Opportunities

- **Expand: R&D forum & other outreach**
- **Leveraging other governmental R&D efforts via collaboration or technical input**
- Interagency group memberships: IAPG, FIMaR, and similar
- **Diversity of research areas**
- Increased organizational involvement
- Updated regulations and guidance
- Increased intermodal involvement, e.g. NHTSA, FAA, FMCSA, FRA
- **Increased Executive engagement**

T

Threats

- Transitions make certain efforts difficult leading to low program performance
- **Growing list of approving authorities in chain**
- **Speed of awarding contracts can be too slow, putting budgets at risk**
- **Uncertainty with budgets puts some initiatives in jeapordy**
- **Project management falls to the few who are CORs; lack of robust PM resources**
- Travel Burden - travel is integral to R&D projects, in particular start and close-out.

SWOT Summary

- While the OHMS R&D program has grown and improved, there are opportunities to continue improving
- Need to expand supplementary functions, including:
  - project management
  - program robustness (review board and increased outreach)
  - travel burden
  - training/succession planning
- Contracting remains slow due to the increased number of players required for project approval
- Growth of the R&D budget would expand its presence and positively affect the overall organization

R&D Program – Next Steps

Follow on meeting with R&D leadership to determine course, path adjustments, timelines and approval process. Findings and feedback will determine initial strategic plan and program structure.

- **Phase 1: commencement of more granularity and subsequent planning steps – Strategic outline**
- **Phase 2: inform R&D community of updated processes, findings, and integrate with Forum objectives – get feedback**
- **Phase 3: Review of information, interface with leadership, and update of strategic plan document**

Thank you

Please provide feedback to us:

- eva.rodezno@dot.gov - Eva
- rick.boyle@dot.gov - Rick
- satyaveda.Bharath@dot.gov - Veda
- https://www.phmsa.dot.gov/research-and-development/phmsa-research-and-development

Appendix

Strength Weakness Opportunities Threats (SWOT) Analysis

Purpose: This analysis was executed to determine the gaps in the current program. It will also inform the areas for improvement and performance measures to address these deficiencies.

The former strategic plan stopped at performance goals and did not reflect the supporting functions and metrics to realize the goals and contribute to the Vision.

PHMSA Development of R&D BAA

PHMSA Issues Broad Funding Announcement

1. Researchers Partner With Stakeholders to Generate Questions

2. Researchers, Stakeholders apply Review Criteria in their applications

3. Peer review prioritizes application by level of alignment with criteria and strategic objectives

Creation of Diverse Research Portfolio Answering Key Research Questions

OHMS 2017 Broad Agency Announcement Status

OHMS R&D Forum
May 16th, 2018
Eva Rodezno, R&D, OHMS

BAA Basics


BAA 4 STAGE PROCESS
1
Expressions of Interest
2
Development of Concept Papers
3
Review Board
4
Determination and Award

BAA Topic Areas

Risk Management:
- Natural gas hydrate packaging
- Shock & impact data for lithium ion batteries (LiBs)
- Improve packaging (mechanical, thermal resistance)
- Mitigating HM packaging rupture

Package Integrity:
- Infectious waste byproduct packaging standard
- Standards for novel materials in bulk packaging
- Standards for non-bulk packaging
- New materials for packaging

Emerging Technologies:
- Exploring the use of UAVs for HM transport
- Smart cities & HM incidents
- Risk analysis of transporting LiBs
- Risk mitigation of energy products transportation

Technical Analysis for Risk Assessments:
- Spill model for LNG
- Classification of damaged LiBs
- Classification of polymerizing materials
- Classification of biofuels

2017 Broad Agency Announcement

Topic Generation → **Gap Confirmation** → **Research Prioritization** → **Final Selection**

Topic Generation

Outreach & Stakeholders
Email
OHMS R&D Web Page
Forums & Conferences

PHMSA
R&D Strategic Plan
Budget Submissions
Program Review & Mgmt

Other
Congress
Modal Partners
TRB, NTSB
Interagency (Jack rabbit)

Gap Confirmation

White papers given internal assessment and evaluated on safety and regulatory gaps identified, current safety demands (special permits), Multimodalism

Research Prioritization

1. PHMSA Topic Review & Disposition
2. Internal Determination or External SME Review
3. Research Prioritized

Final Selection

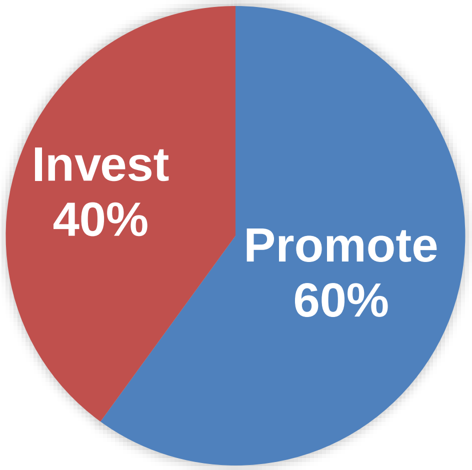
1. PHMSA Mgm't Determination and Concurrence
2. Contract Award

2017 BAA Contract Status

- OHMS received 80+ white papers totaling $39M
- 30+ white papers accepted and full proposals requested Sept 2017
- Approximately 15 full proposals accepted, totaling $7M
- Final proposals selected March 2018
- 2-year funded projects

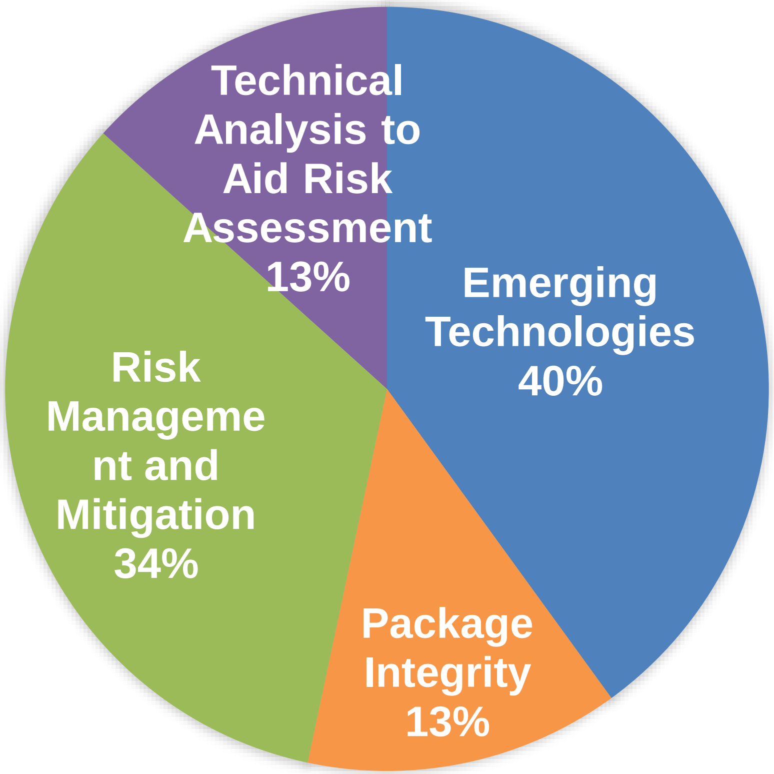
80+ white papers → 30+ full proposals → ~15 projects

Selected BAA Proposals & PHMSA Goals

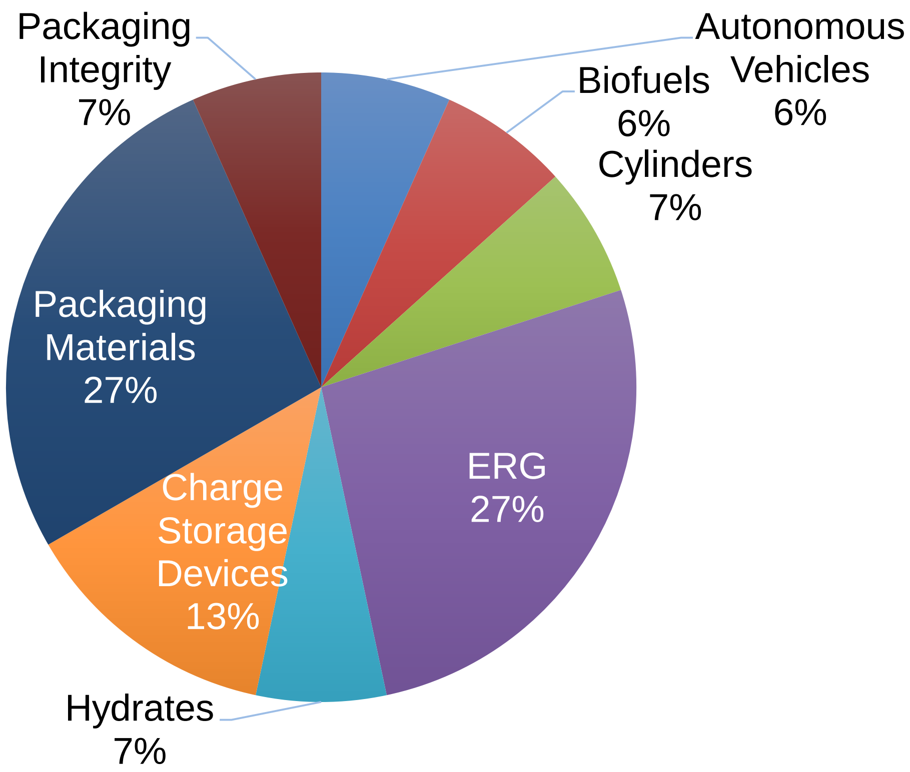


- **Promote continuous improvement in safety performance**
- **Invest in safety innovation to become more proactive and forward-looking**
- Build stakeholder and public trust
- Cultivate organizational excellence and safety culture
- Pursue operational excellence

Selected BAA Proposals & OHMS Goals



Selected BAA Proposals & Technology Type



Lessons Learned from 2017 BAA

- Need to do a better communicate our broad area of need
- Should emphasize the need for experimental work where it is most appropriate
- Assign a general priority with each topic area
- Investigate faster acquisition strategies

Summary

- ~15 proposals chosen, totaling $7M
- Heaviest hitters:
  - ERG
  - Packaging Material
  - Charge storage devices
- Too early to predict when next BAA will be announced
- OHMS will likely format and conduct next BAA differently

Thank you!

- https://www.phmsa.dot.gov/research-and-development/hazmat/research-and-development-branch

- eva.rodezno@dot.gov
- rick.boyle@dot.gov

CARDEROCK DIVISION

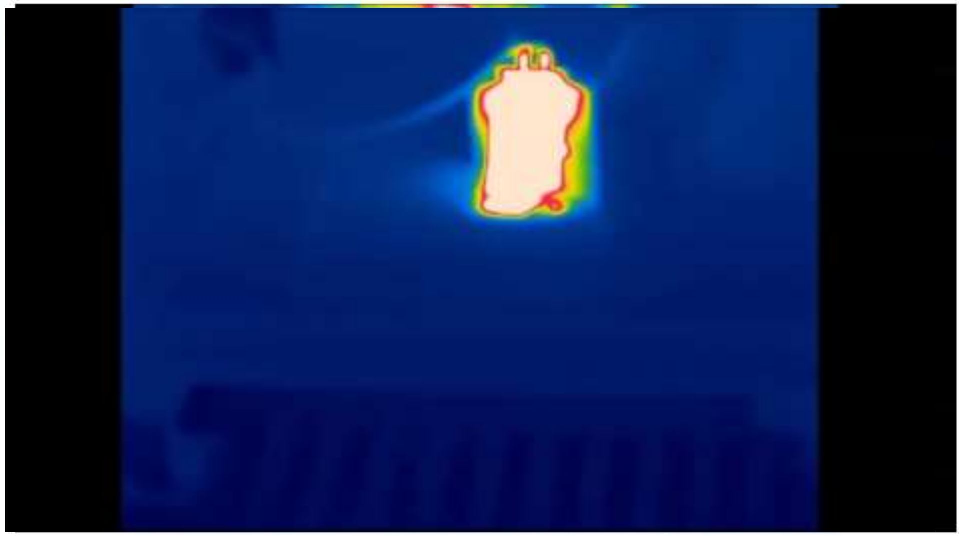
Lithium Battery Safety: Failure Prevention and Mitigation During Transport

Presenter: *Jonathan Ko, PhD*
Lithium Battery Research Team
Advanced Power and Energy Branch

NAVSEA WARFARE CENTERS

US DoT PHMSA HazMat R&D Forum *16 May 2018*

High Temperature Abuse of Commercial Cell Phone



- Thermal runaway occurred with temperatures exceeding 380^{o}C.
- Battery vented, releasing flammable solvent.

High Temperature Abuse 500Wh Battery Pack

Hazards of Lithium Batteries

- Batteries are stored chemical energy

- Controlled release of this energy provides electrical power in the form of current and voltage

- Uncontrolled release of this energy can result in venting, fire, release of toxic materials, shrapnel, high pressure events, deflagration (with or without report) and many combinations thereof

Navy’s Lithium Battery Safety Program

- Lithium batteries provide substantial increases in both gravimetric and volumetric energy density over other commercial battery types
- Seven personal injuries were reported from 1976-1983, including one death
- DoD issued a policy stating that lithium battery hazards would have to be managed if the technology was going to be utilized
- All lithium batteries used by Navy/Marine Corps personnel must be approved for use through Navy’s Lithium Battery Safety Program
- NSWC Carderock is a Technical Agent of this Program, providing technical expertise in lithium battery safety to the Navy and Marine Corps

Lithium Batteries and the DoT PHMSA Mission

NAVSEA WARFARE CENTERS Carderock

Mission & Goals

Our mission is to protect people and the environment by advancing the safe transportation of energy and other hazardous materials that are essential to our daily lives.

Update: Statement from Fisker Karma owner


ABC News


ABC News

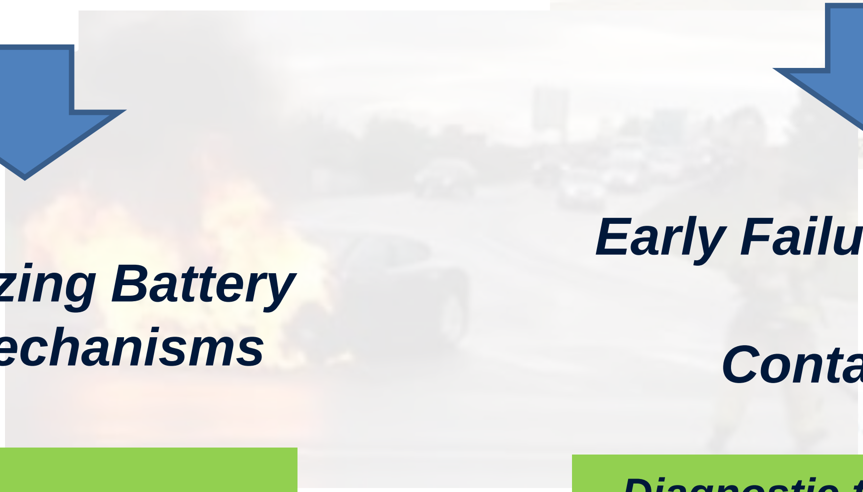

http://techbakbak.com/hoverboards-setting-homes-fire/

U.S. Department of Transportation

PHMSA

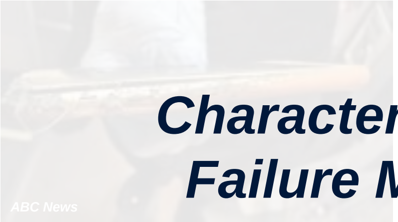
Pipeline and Hazardous Materials Safety Administration

Lithium Battery Priorities for DoD and DoT PHMSA

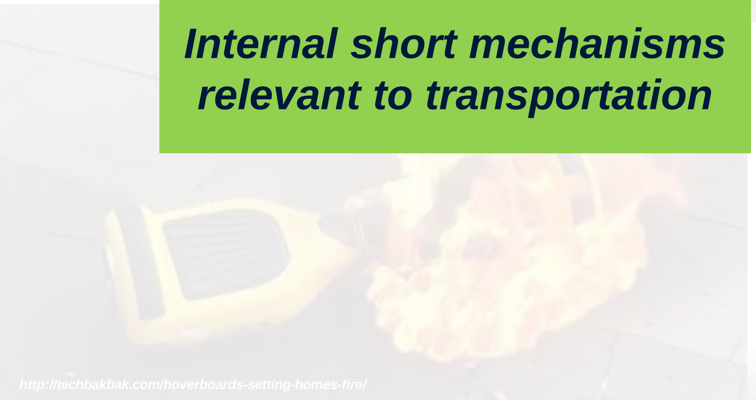


Hazard Identification and Prevention

Characterizing Battery Failure Mechanisms



Internal short mechanisms relevant to transportation



Hazard Mitigation

Early Failure Detection

+

Containment

Diagnostic technologies for advanced notice of failures

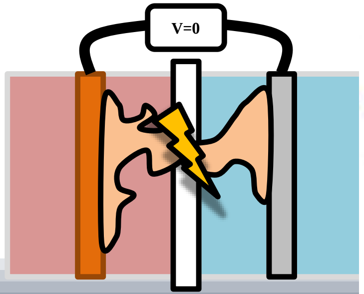
Hazard Identification and Prevention

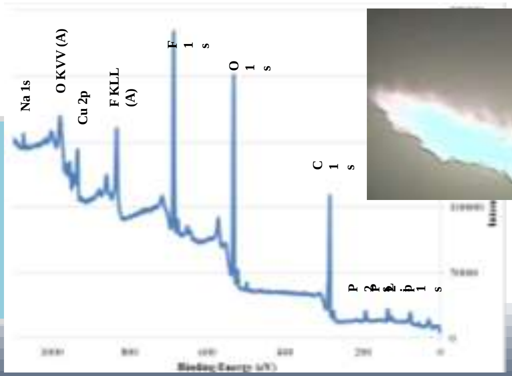
Lithium Battery Failure Mechanisms

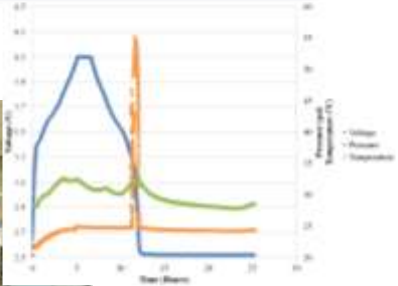
The transportation industry remains vulnerable to occurrences of low probability, high impact latent cell defects that can trigger internal short circuits in the absence of an associated hazard event. Understanding delayed cell failure mechanisms will inform future protections against failure.

Objectives:

- Examine onset of lithium plating, condition of the SEI layer, and copper dissolution thresholds in lithium ion batteries
- Provide mechanism-specific indicators relevant to sequence of events and root cause failure of lithium battery related transportation incidents







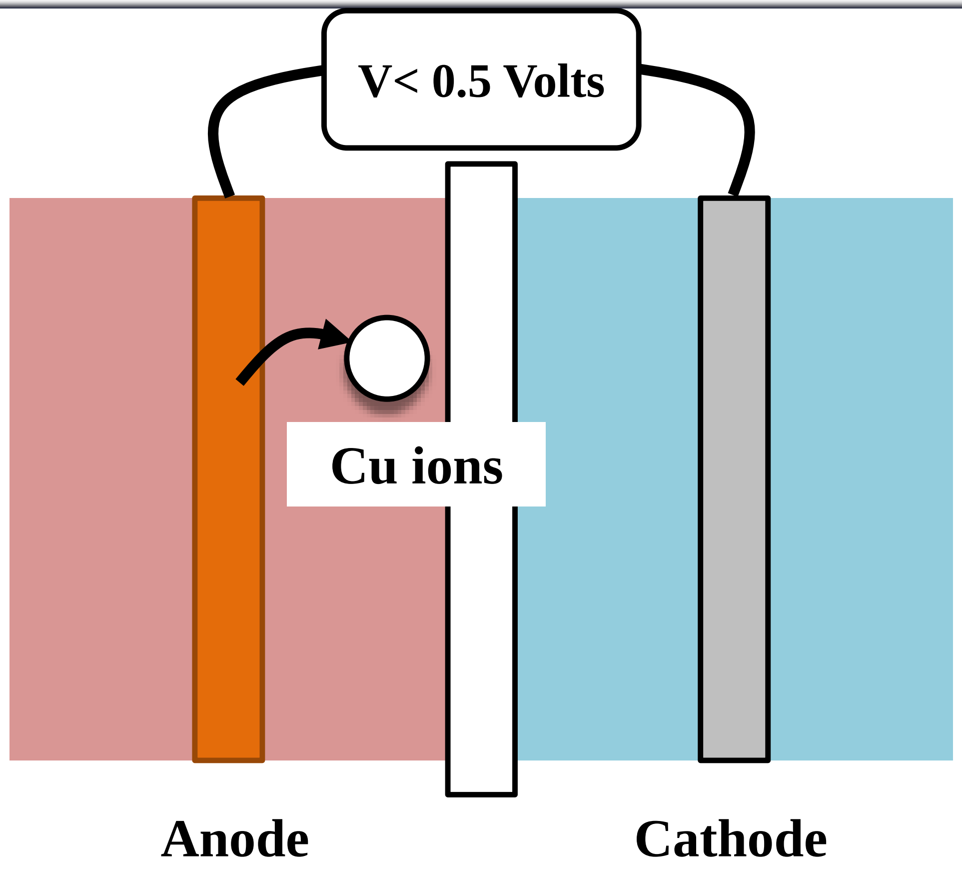
Approach

- Lithium-ion batteries are used in a variety of applications.
  - ➢These batteries can sit unused for long periods of time and are expected to perform safely as part of multi-cell packs.
  - ➢As a result, overdischarge is one failure mechanism of interest.

- To address concerns about overdischarge and subsequent charge on lithium-ion battery safety:
  - ➢Large format lithium-ion cells were disassembled in overdischarged and “healthy” states.
  - ➢X-ray photoelectron spectroscopy (XPS) was used to:
    - Measure copper dissolution, migration, and re-precipitation on electrode surfaces.
    - Investigate the SEI layer on the anode

Copper Dissolution

- Copper dissolution can occur when the potential of the anode vs. Li^+/Li is approximately 3.4 Volts [1].
  - In a full cell, this corresponds to a cell voltage approximately 0.5 Volts or below, depending on cathode chemistry and anode/cathode active material ratios.
- Copper dissolution and migration has been studied in beaker cells [2-5] and small-format lithium-ion cells [6].



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3. *M. Zhao et al., Journal of the Electrochemical Society, Vol. 147 (11) (2000) pp. 3983-3988.*
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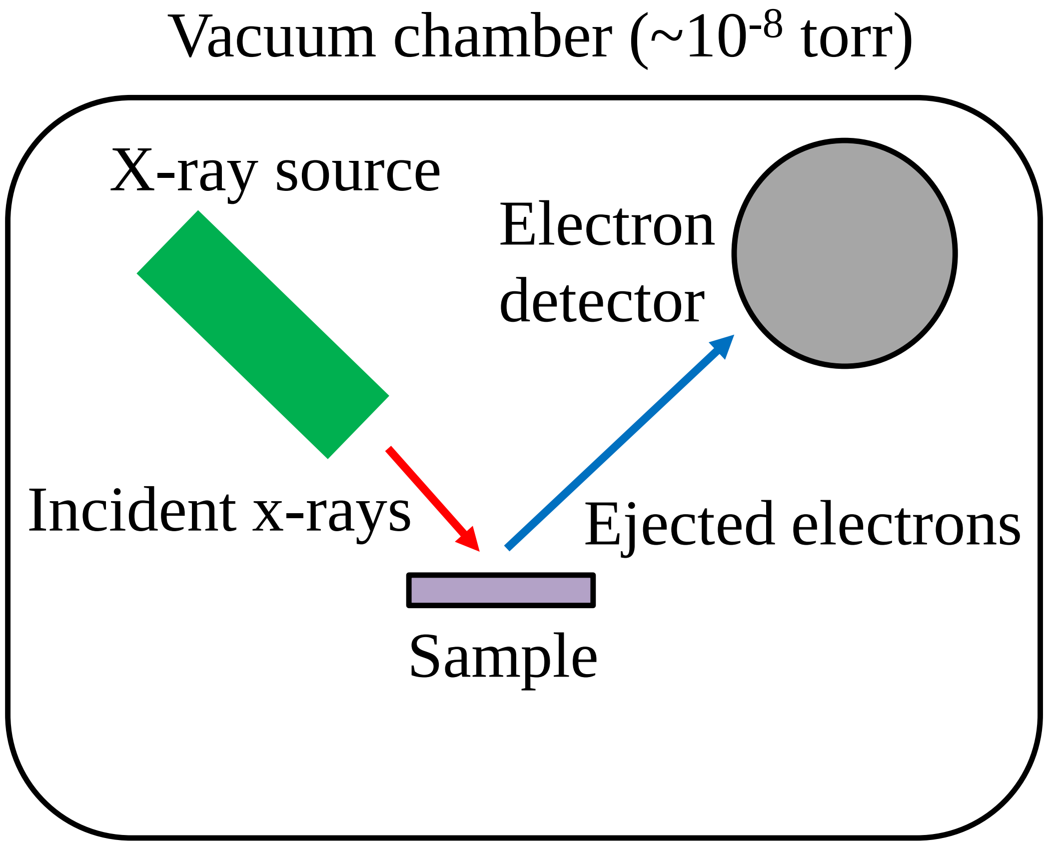
6. *H. Maleki and J. N. Howard, Journal of Power Sources, Vol. 160 (2006) pp.1395-1402.*

X-Ray Photoelectron Spectroscopy

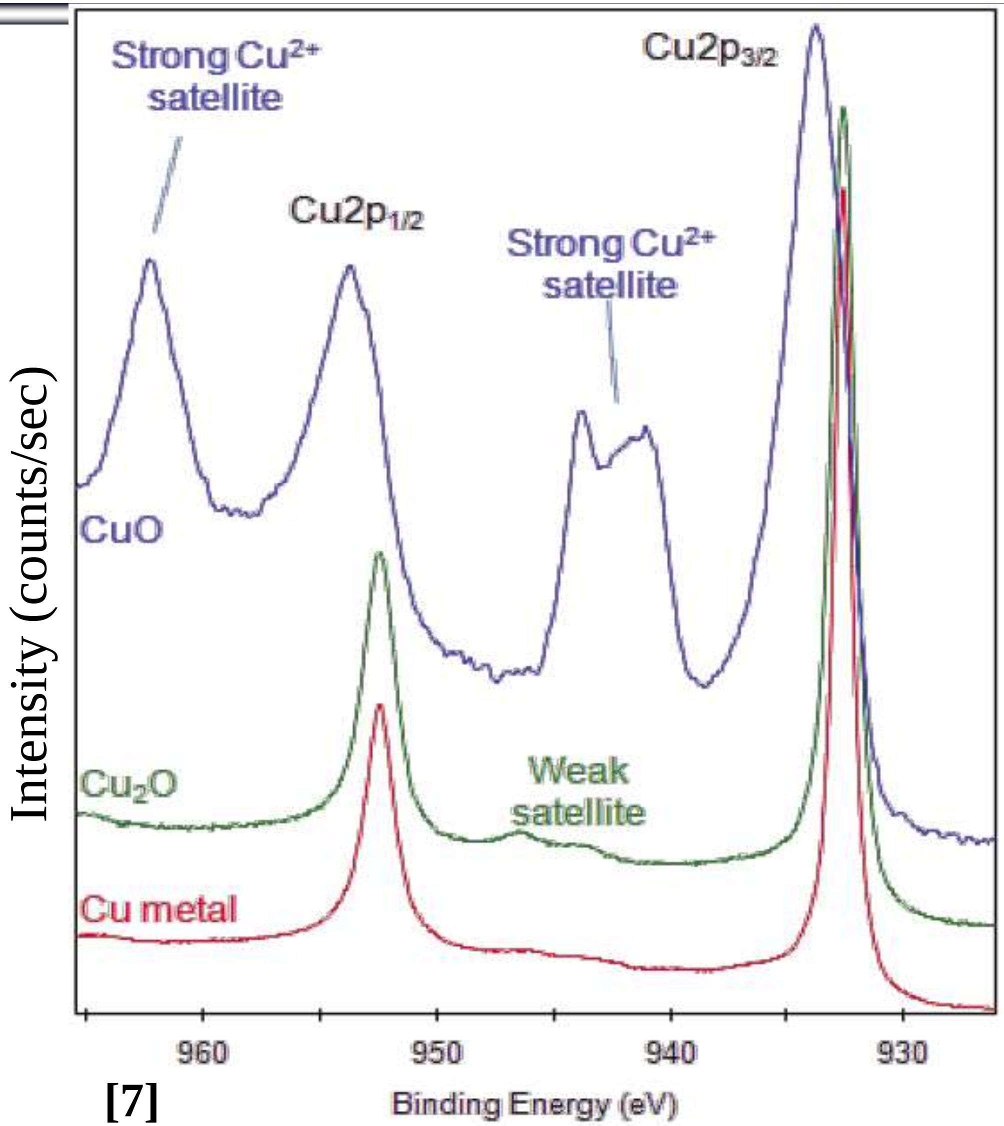


$$BE = h\nu - KE$$

Known x-ray energy **Kinetic energy measured by detector**

- XPS is a surface analysis technique
  - Provides elemental and chemical state information
  - Combined with depth profiling (Argon/C60 sputtering) gives concentration as a function of depth from the surface

Sample XPS Spectra - Copper



[7]

- XPS measurements provide a reading of peak intensity vs. binding energy.
  - Differences in the measured spectra allows for the identification of unknown compounds.

Species	Binding Energy (eV)	FWHM (eV)
Cu	932.5	1.1
Cu_2O	932.5	1.2
CuO	933.8	2.9

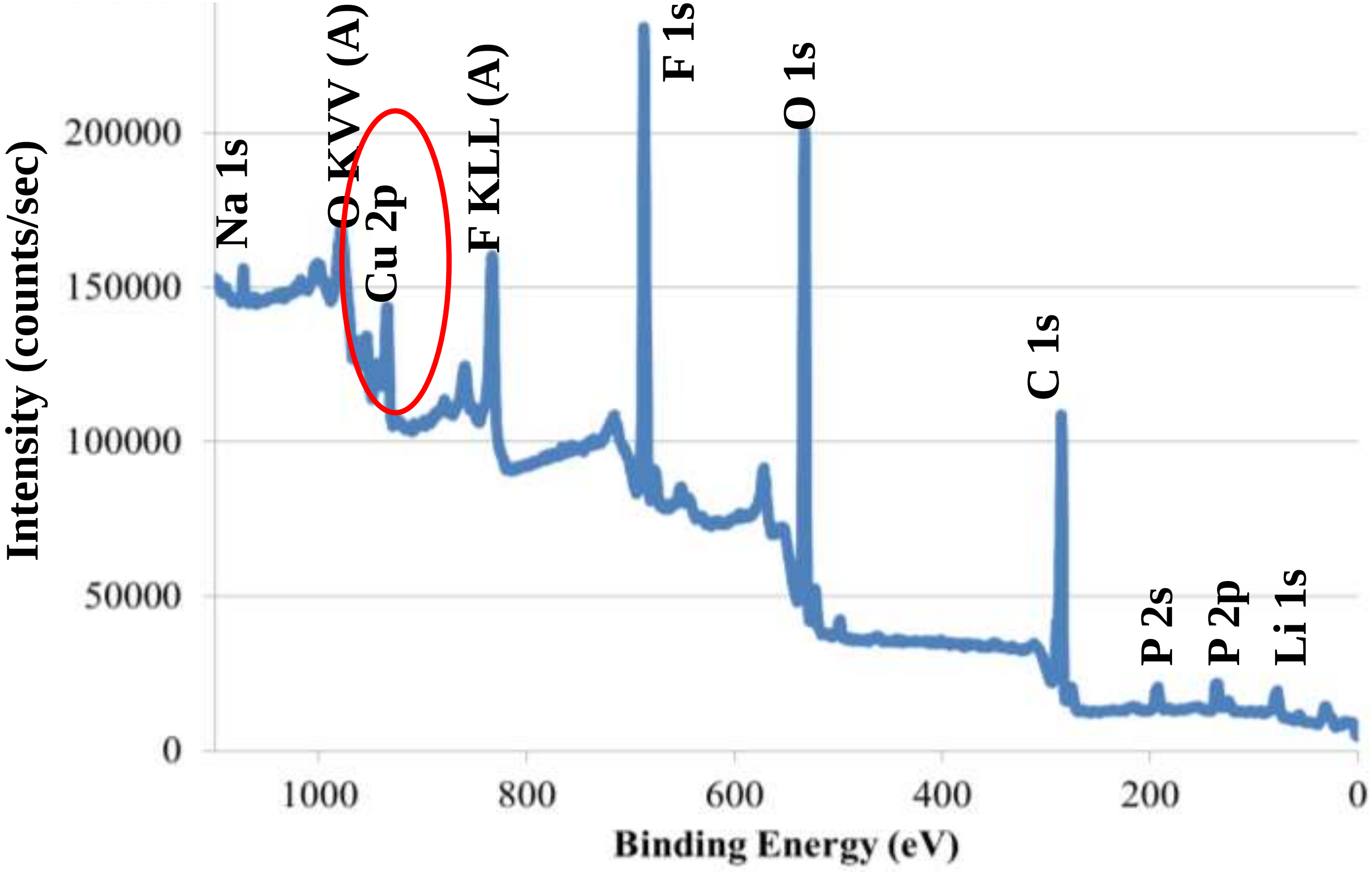
XPS of 2.5 Volt cell

	Anode (Atm%)			Cathode (Atm%)		
Element	Exterior	Middle	Interior	Exterior	Middle	Interior
Li / 1s	21.3	23.4	22.3	11.1	7.7	11.6
C / 1s	33.5	26.3	27.3	40.9	42.8	38.8
O / 1s	28.5	23.5	23.4	12.9	13.2	12.8
F / 1s	14.3	23.5	23.7	33.9	34.9	35.2
Na / 1s	0.6	1.1	0.9	0.4	0.6	0.4
P / 2p	1.8	2.3	2.4	0.8	0.9	1.2
Cu / $2p_{3/2}$	0	0	0.1*	0	0	0

*Some of the copper current collector may have been exposed, resulting in a very weak signal.

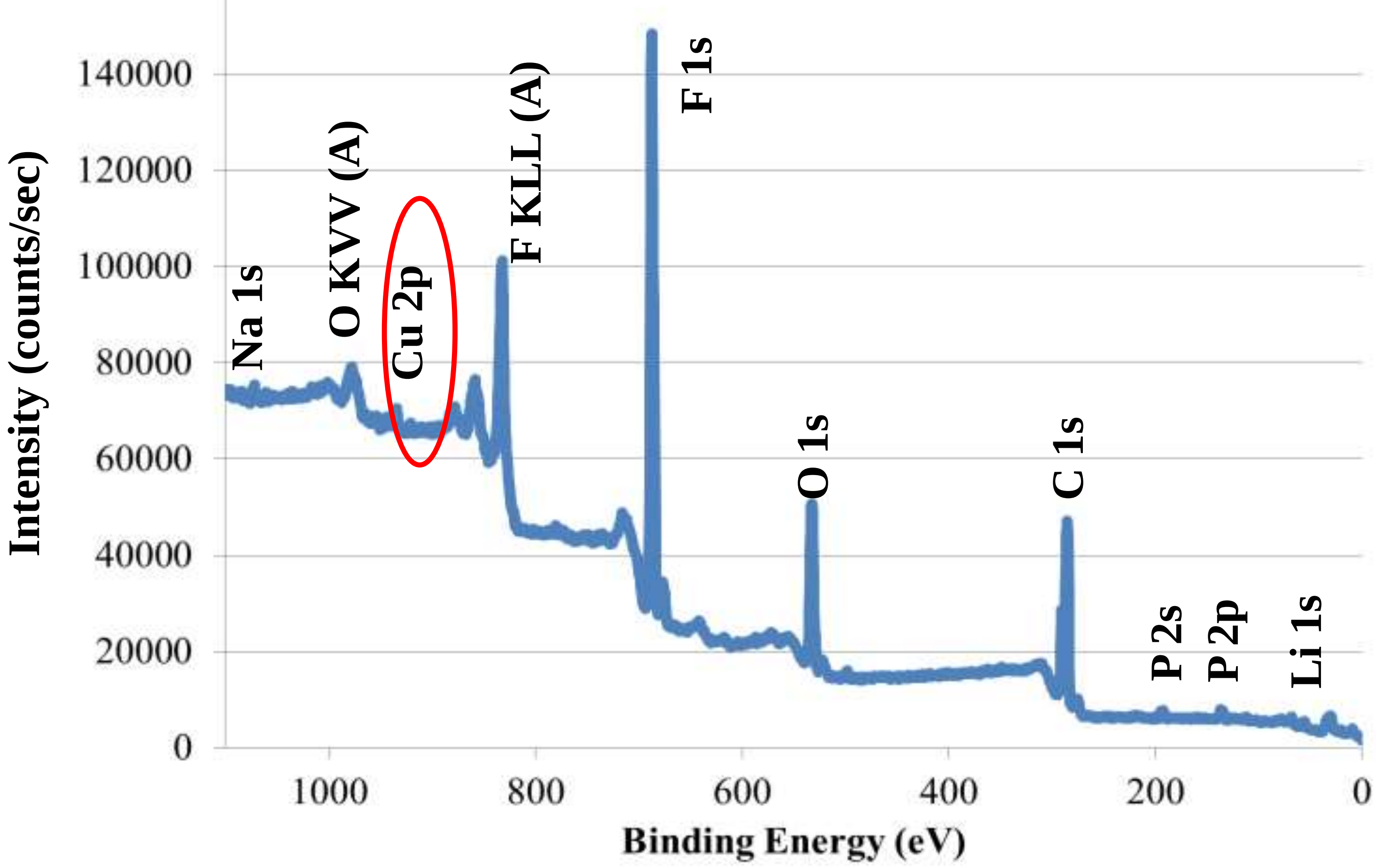
XPS Anode Exterior (0 Volt cell)

Element	Li / 1s	C / 1s	O / 1s	F / 1s	Na / 1s	P / 2p	Cu / $2p_{3/2}$
Atomic %	9.9	38.2	25.2	19.6	1.1	2.7	3.3



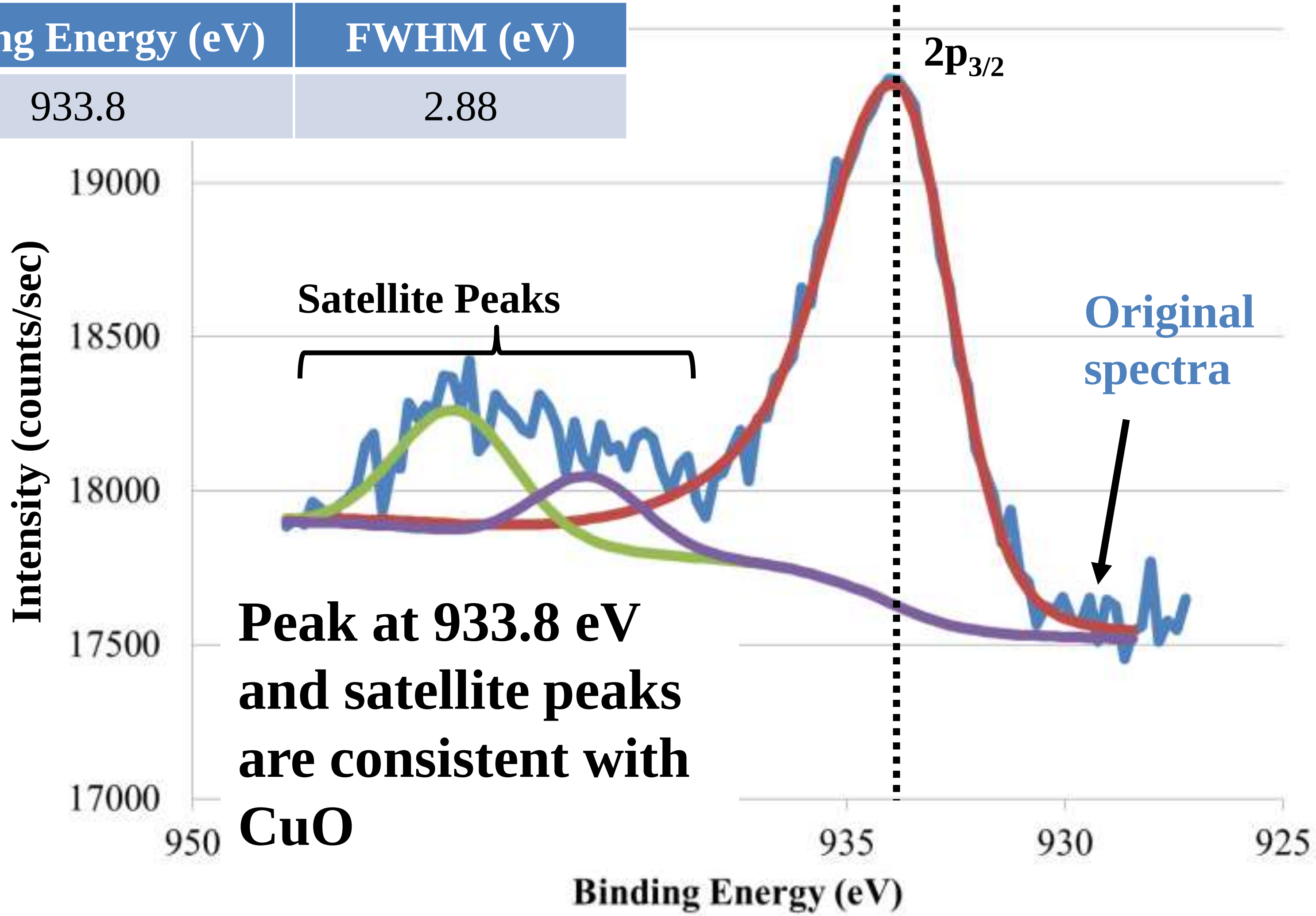
XPS Cathode Exterior (0 Volt Cell)

Element	Li / 1s	C / 1s	O / 1s	F / 1s	Na / 1s	P / 2p	Cu / $2p_{3/2}$
Atomic %	10.9	41.5	13.2	32.1	0.4	1.0	0.9



XPS of Cu $2p_{3/2}$ (0 Volt Cathode)

Binding Energy (eV)	FWHM (eV)
933.8	2.88

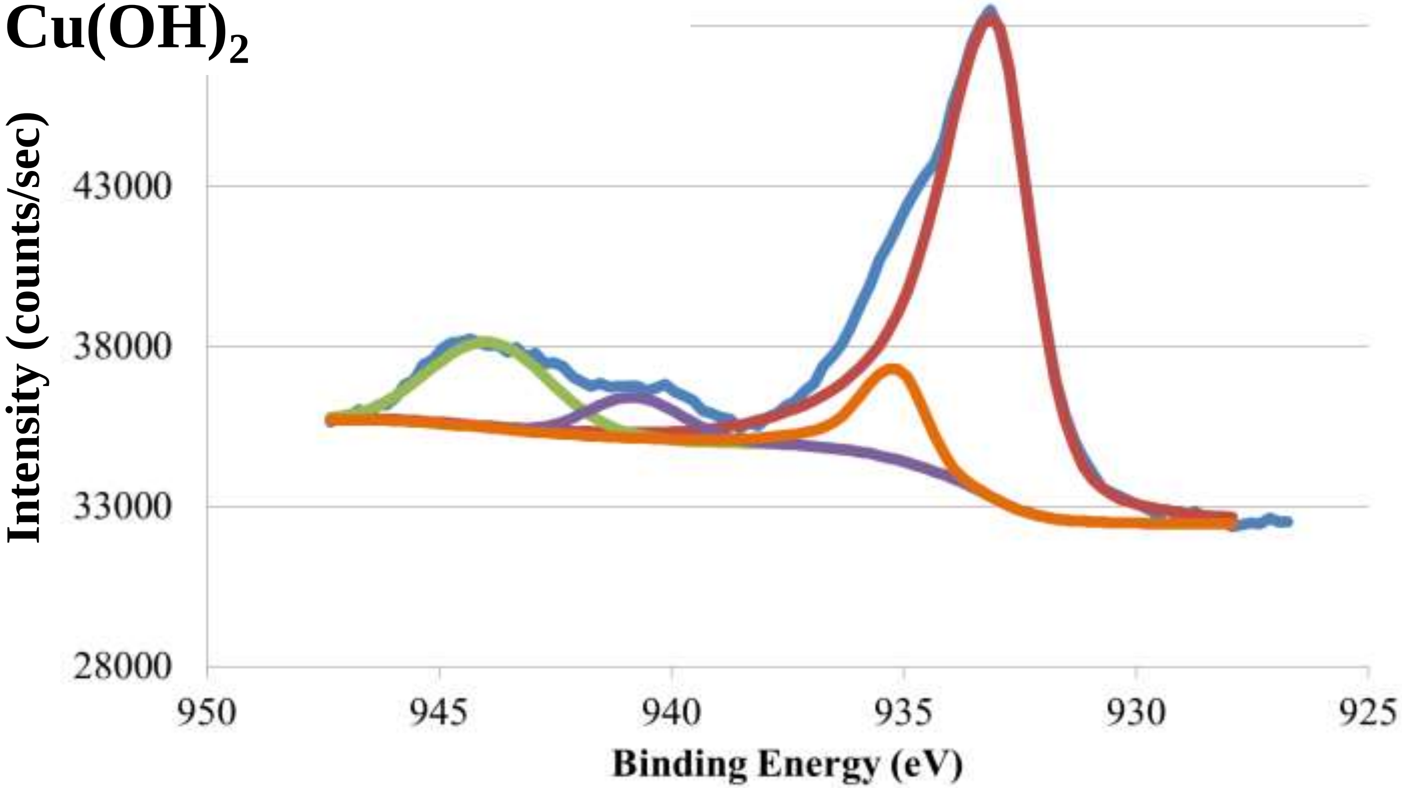


Peak at 933.8 eV and satellite peaks are consistent with CuO

XPS of Cu $2p_{3/2}$ (0 Volt Anode)

Peaks for anode are a little less clear for the chemical state. Species could include CuO, CuF_2, $Cu(OH)_2$

Binding Energy (eV)	F WHM (eV)
933.1	1.9
935.2	1.5



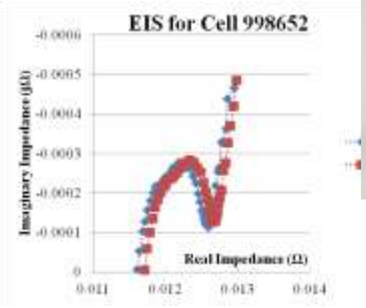
Hazard Mitigation/Containment

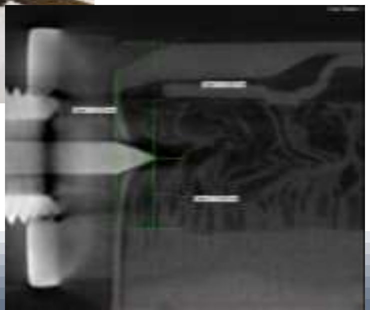
Diagnostic Technologies for Battery Failures

The energy density of bulk packages of lithium batteries presents challenges for containment of failure events. Detection technologies that detect failure events earlier can inform choice of mitigation technologies and activate mitigation earlier to improve effectiveness.

Objectives:

- Assess effectiveness of emerging technologies for detecting internal short conditions in cells prior to a thermal runaway event
- Evaluate practicality of technologies for transportation industry





A Priori Detection Options

Voltage, temperature, current

Particulate emission

Gas emissions (VOCs, electrolyte vapor)

Electrical, magnetic fields

Strain-Pressure

Thermal, acoustic, optical properties

Moisture

Resistance and Impedance

Other?

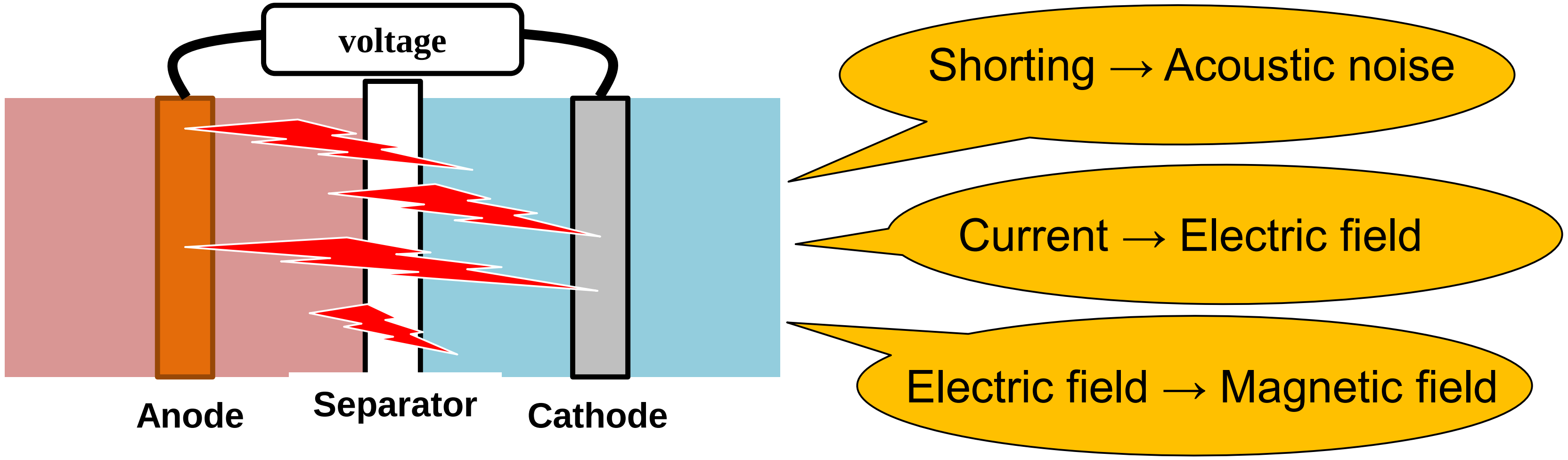
Remote Detection Technologies

- **Chemical Sniffing**

  - Miniaturized VOC, electrolyte detection; spectroscopy
  - Prototypes currently under development by industry
  - Limited Navy testing to-date
    - chemical/environment compatibility under evaluation
  - May operate remotely, sans interface with battery
  - May be integrated to supplement traditional battery BMS
  - Location exterior to battery pack correlates to detection after cell failure, electrolyte leakage

Physics Based Remote Detection Technologies

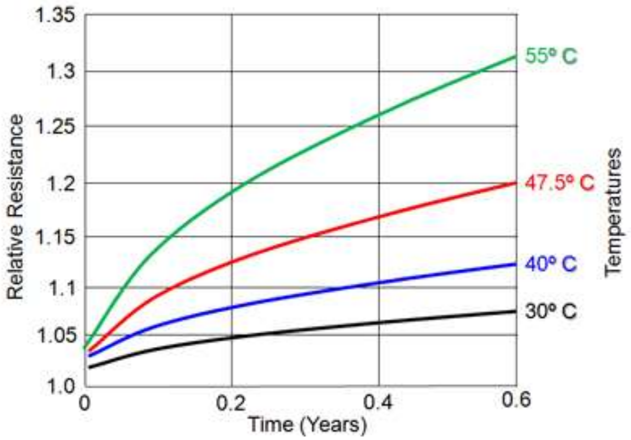
- **Remote sensing of internal shorts**

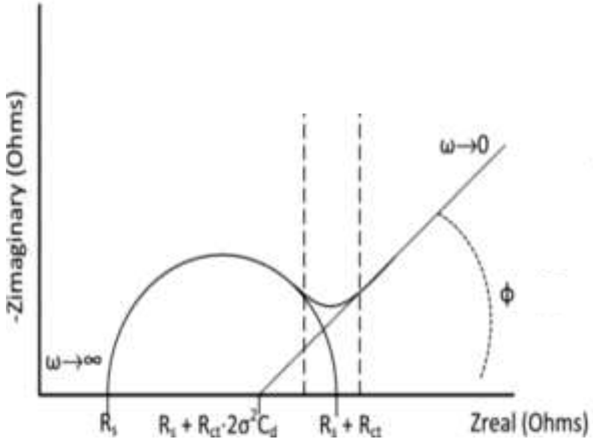


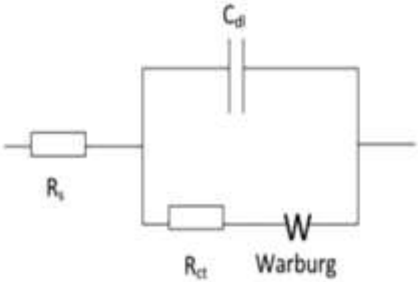
  - Electrical, magnetic, acoustic changes
  - Prototypes currently under development by industry
  - May operate remotely, sans interface with battery
  - May be integrated to supplement traditional battery BMS
  - Detection dependent on location, proximity to system

Battery Integrated Detection Technologies

- **Resistance and Impedance Monitoring**







- **DC and AC response, battery and cell**
  - In-situ Electrochemical Impedance Spectroscopy (EIS) – internal resistance
- **Prototypes under development by government and industry**
- **Demonstrated early detection of overcharge and short**
- **Requires electrical interface with battery/cells, initial characterization of cell/battery to establish acceptable ranges, some prototypes require steady-state (sec to hrs) to take measurement**

Battery Integrated Detection Technologies

- **Strain – Pressure – Gas generation, volume change or voltage signature internal/external**

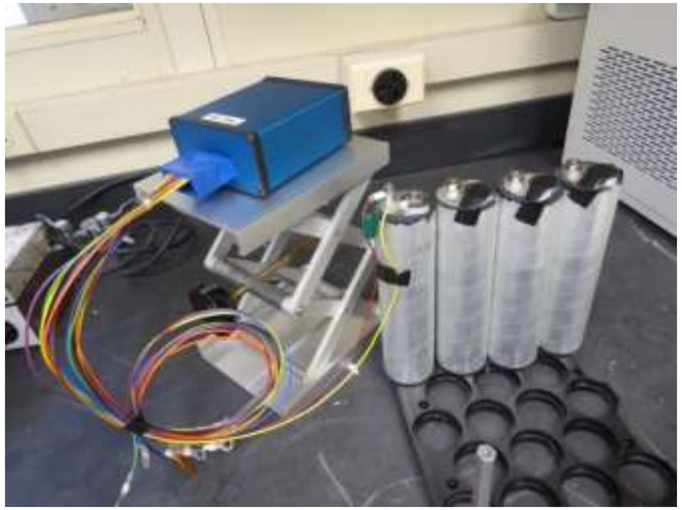
- **Recent proposed separator sensor to detect Anode2Sep or Cathode2Sep dendrite formation and current flow**
- **Strain gauge or fiber-optic sensor to sense gas generated or temperature**
- **Government and industry prototype development**
- **Demonstrated in-situ correlation between strain gauge, gas generation, and health;**
- **Requires integration interior to cell; exterior to cell or battery**

http://batteryuniversity.com/learn/archive/pouch_cell_small_but_not_trouble_free

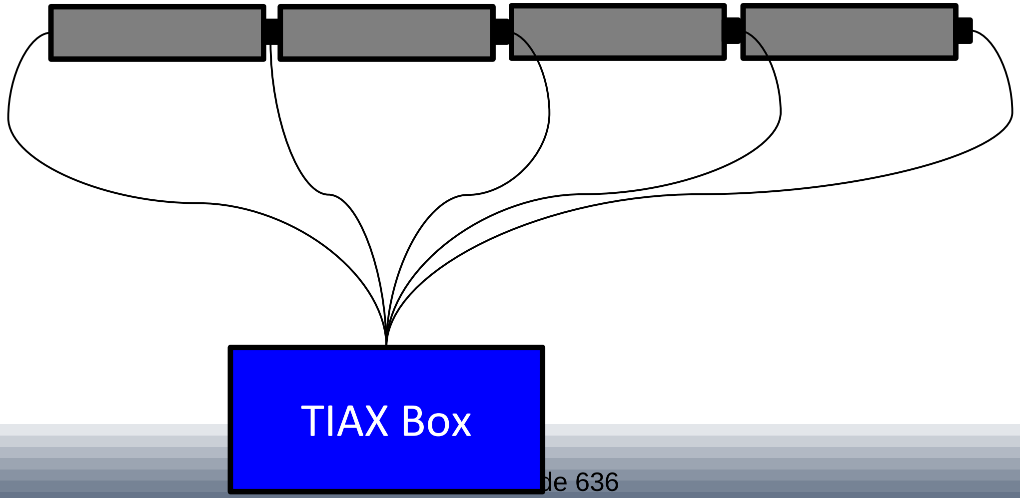
Technologies Planned For Evaluation by NSWC Carderock

- INL/Sandia – agreement to test
- NRL prototype – agreement to test
- JHU APL prototype – under test
- TIAX – under test
- Luna/Nexceris – testing for Navy program under separate effort (transition agreement)
- Carderock modeling – ongoing
- Parthian – agreement to test
- Redondo Optics, PARC, Feasible, others of interest

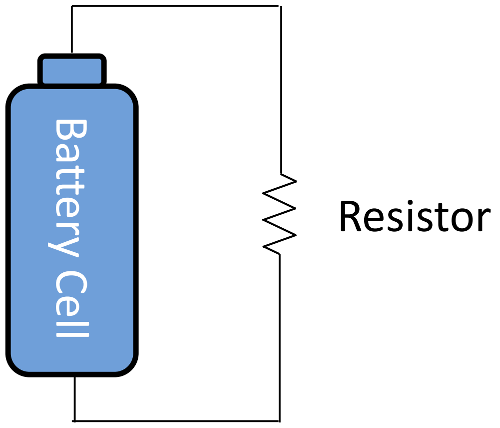
TIAX "Blue Demo Box" (1st Gen, Universal Detection Technology)



- Has 13 test leads that can test up to 12 cells sequentially.



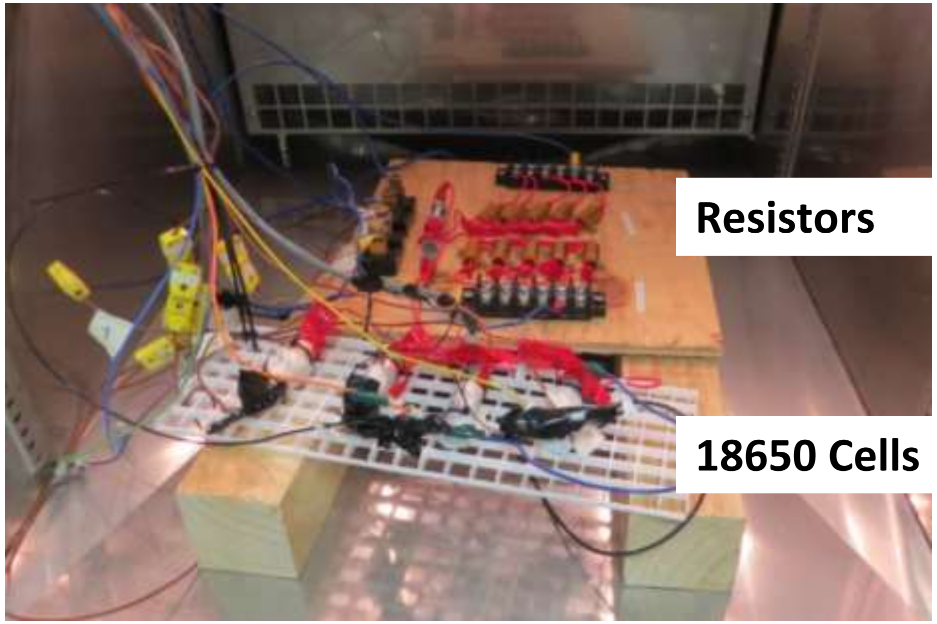
TIAX "Blue Demo Box"
(1st Gen, Universal Detection Technology)

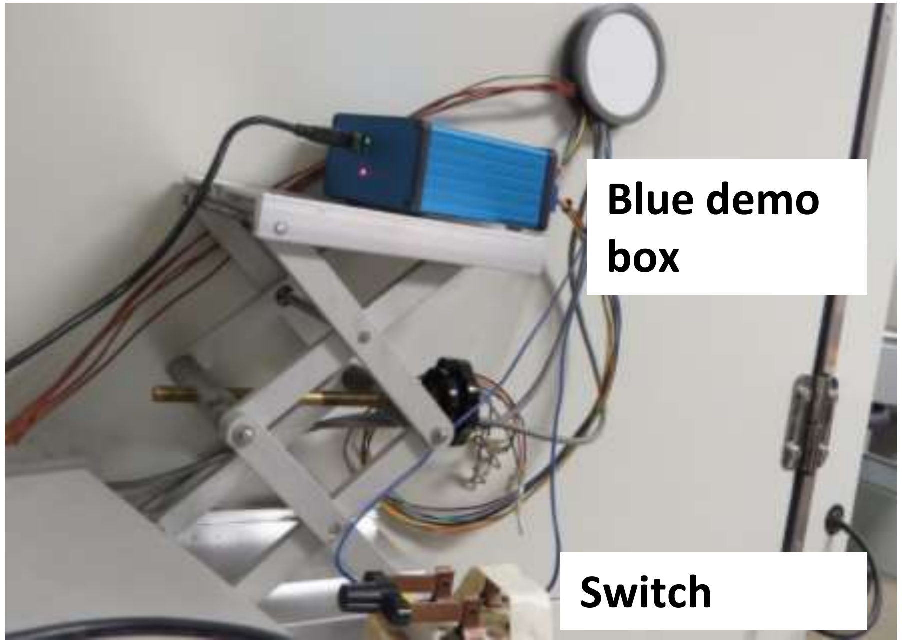


Resistance of Short	Score
No short	-5.361
500 Ohms (6-8mA)	12.535
400 Ohms	16.481
300 Ohms	22.153
200 Ohms	36.319
100 Ohms (30-40mA)	83.319
No Short, After Test	-5.147

- Resistors are used to simulate different level shorts
- Different score numbers are generated by applying different resistance

Test Setup TIAX Blue Demo Box





- Cells are placed in a temperature controlled oven
- Shorts are applied to the cell and measurement was taken immediately when the short is applied and after 15 mins

18650 Cell Simulated Short @ 25°C

- Blue demo box was able to detect the different level of short.
- Multiple scan of the same short level will yield slightly different score numbers
  - Each short level will have a different score range
  - Score numbers can overlap different short levels
- TIAX has done some modeling to determine the short level that could cause a battery failure
- The demo box can distinguish 500Ω and below simulated shorts

Short	Score
No Short	-4.726
500	20.885
400	26.654
300	38.287
200	58.375
100	120.50
No Short	-5.198

Scan immediately applying short

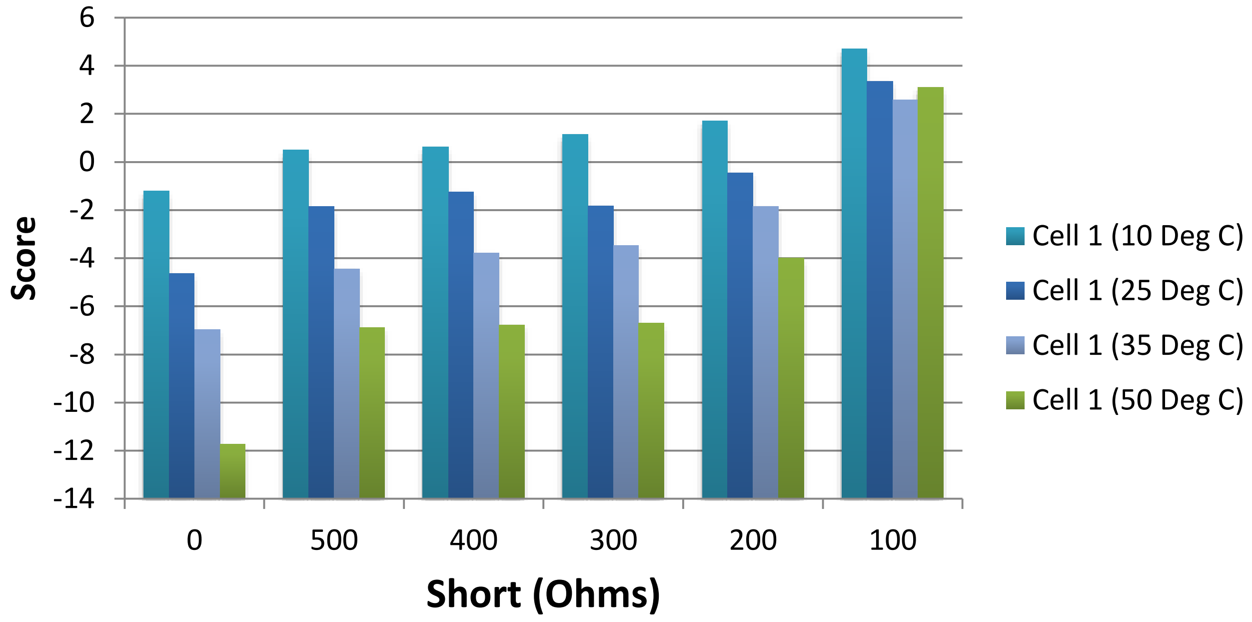
Short	Score
No Short	-4.726
500	-1.053
400	-1.141
300	-0.371
200	1.486
100	5.071
No Short	-5.198

Scan 15 mins after applying short

Effects of Different Internal Temperature

- In order to determine how the temperature of cells affect the early prevention device, 18650 cells were soaked at different temperature (10, 25, 35, 50° C) for 1-2 hours.
- Simulated shorts were applied to the cells and measured with the blue box.

Effects of Different Internal Temperature

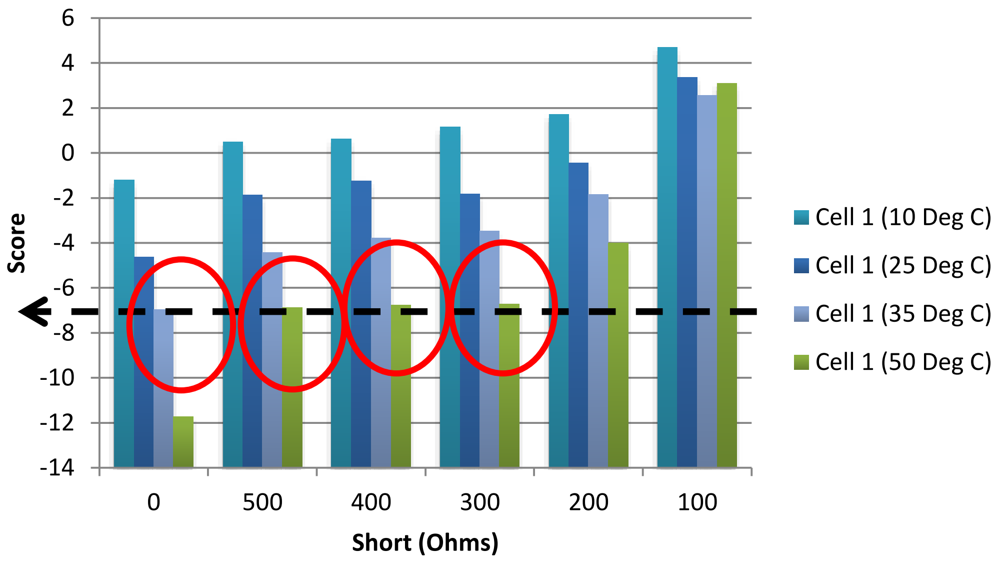


Scan 15 mins after applying short

Temperature	No Short	500	400	300	200	100
10	-1.207	0.493	0.637	1.153	1.717	4.711
25	-4.630	-1.857	-1.242	-1.821	-0.44	3.362
35	-6.965	-4.433	-3.790	-3.470	-1.845	2.545
50	-11.739	-6.885	-6.767	-6.708	-4.000	3.113

Effects of Different Internal Temperature

An unhealthy cell at 50° C may be considered healthy at 35° C



Scan 15 mins after applying short

Temperature	No Short	500	400	300	200	100
10	-1.207	0.493	0.637	1.153	1.717	4.711
25	-4.630	-1.857	-1.242	-1.821	-0.44	3.362
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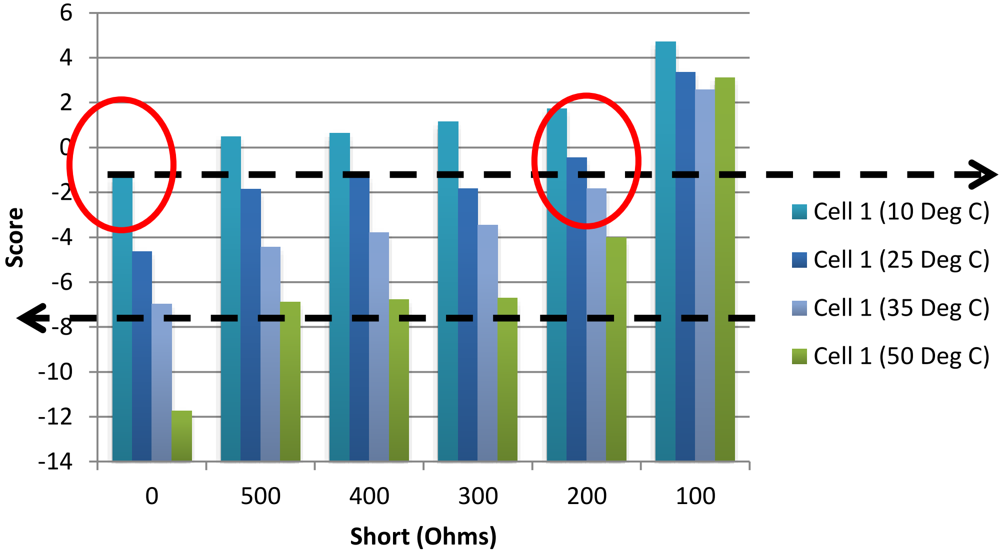
Effects of Different Internal Temperature

An unhealthy cell at 50° C may be considered healthy at 35° C

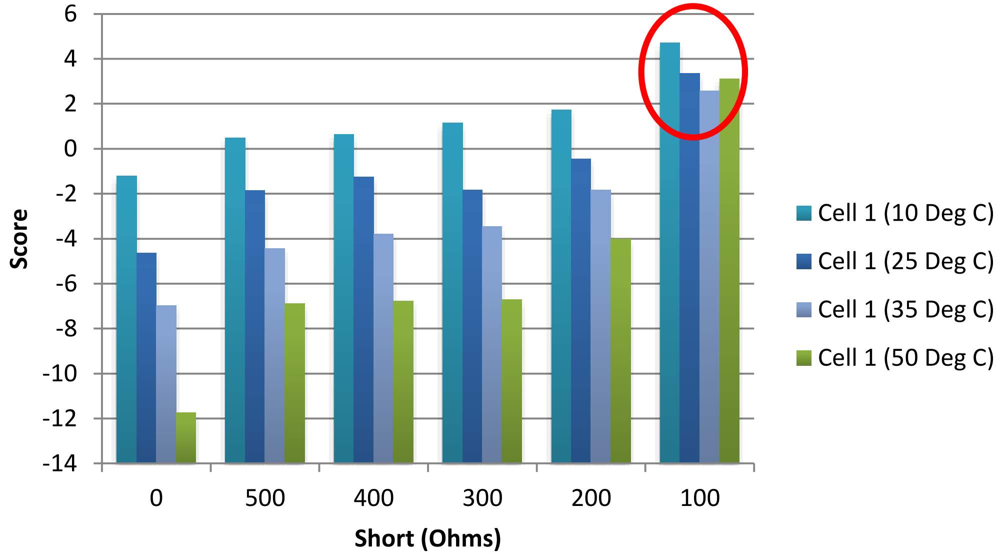


A healthy cell at 10° C may be considered unhealthy at 25° C

Scan 15 mins after applying short

Temperature	No Short	500	400	300	200	100
10	-1.207	0.493	0.637	1.153	1.717	4.711
25	-4.630	-1.857	-1.242	-1.821	-0.44	3.362
35	-6.965	-4.433	-3.790	-3.470	-1.845	2.545
50	-11.739	-6.885	-6.767	-6.708	-4.000	3.113

Effects of Different Internal Temperature



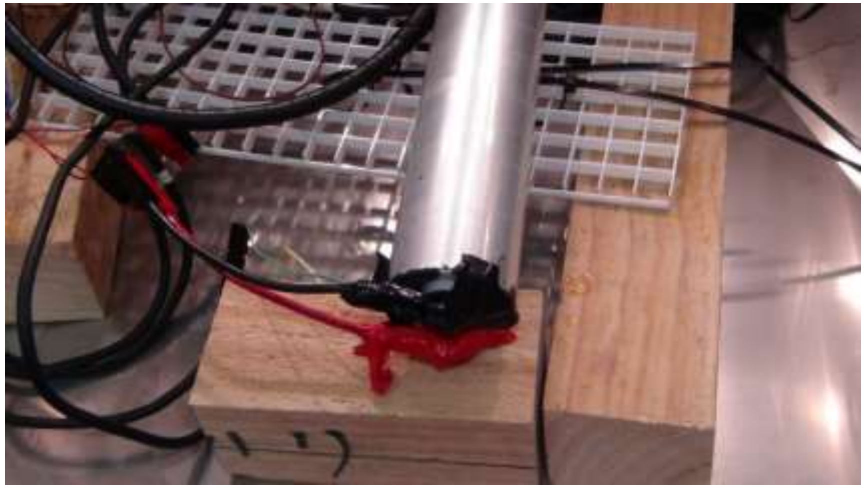
100Ω short is distinguishable compared to the lesser shorts

Scan 15 mins after applying short

Temperature	No Short	500	400	300	200	100
10	-1.207	0.493	0.637	1.153	1.717	4.711
25	-4.630	-1.857	-1.242	-1.821	-0.44	3.362
35	-6.965	-4.433	-3.790	-3.470	-1.845	2.545
50	-11.739	-6.885	-6.767	-6.708	-4.000	3.113

Large-format Cell Simulated Short @Ambient Temp

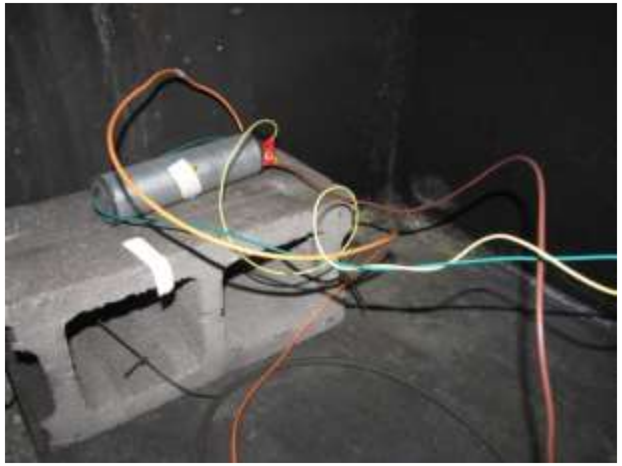
- With this setup it is difficult to determine shorts that are greater than 100 Ω
- Need to explore cell design between 18650 and these large format cells
  - Plan on expanding testing to other cell designs



Short	Score
No Short	-30.813
500	-31.792
400	-33.785
300	-31.693
200	-30.661
100	-19.585

Scan 15 mins after applying short

Large-format Cell – Testing abused cells



- Collection of healthy cell were left in storage in an overdischarged state (0V, 0.25V, 0.5V)
- After 6-8 months, cells were removed charged to 3.6V (50%SOC).
- Blue demo box was used to determine the state of health

Voltage storage	Storage Length	Score at 3.6V	Equivalent short
3.6V	-	-30.813	-
0.5V	6 Months	-31.311	>100
0V	8 Months	-10.161	<100

POCs and Collaborators

- NSWC Carderock Research Team
  - POC: Dr. Jonathan Ko, Jonathan.Ko@navy.mil, 301-227-2955
  - Mr. Tom Jiang, research chemist
  - Dr. Azzam Mansour, electrochemical research SME
  - Dr. Daphne Fuentevilla, research chemist
  - Mr. Christopher Hendricks, UMD doctoral candidate
- Collaborators
  - Naval Research Laboratory (Dr. Corey Love)
  - Expeditionary Energy Office, USMC
  - NSWC Indian Head
  - Industry collaborators

POCs and Collaborators

Dr. Veda Bharath and Ms. Eva Rodezno for their support in the project

“Trigger Mechanisms Leading to Internal Short Circuit and Thermal Runaway”

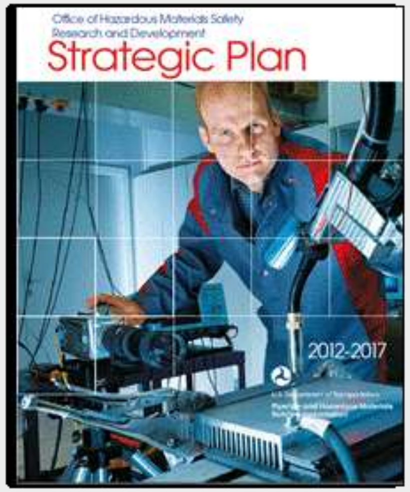
DTPH5616X00007

Corey T. Love, PhD
Chemistry Division, US Naval Research Laboratory

HAZMAT R&D Forum
Washington, DC
16 MAY 2018

Safe Transportation of Hazardous Materials

OHMS, Research and Development Strategic Plan for 2012-2017



"SIGNIFICANT R&D Initiative: greatest impact on safety mission to address immediate hazard within transportation systems."

U.S. NAVAL RESEARCH LABORATORY

- trigger mechanisms
- diagnostics
- prototyping

Reduce Consequences if Incident Occurs

Establish Policy

PHMSA

U.S. Department of Transportation
Pipeline and Hazardous Materials Safety Administration

Conduct Research to Prevent Incidents

Set/Enforce Standards

NAVSEA NAVAL SEA SYSTEMS COMMAND

- large-scale testing
- risk management
- shipping guidance

Lithium Battery Safety Research Programs Must Encompass:

PREVENTION → MITIGATION → CONTAINMENT

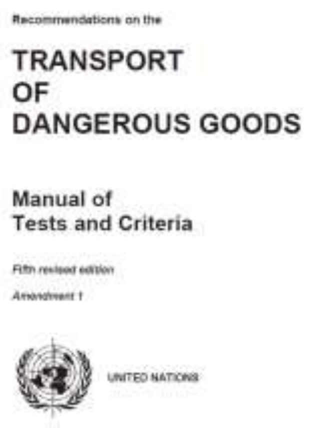
Outline of Research Efforts FY16-18

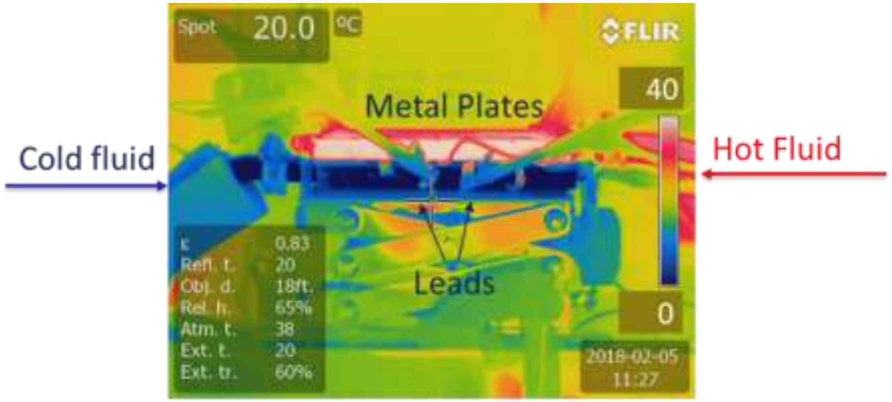
- Internal short circuit triggering mechanism.
- Battery monitoring device (**Bat**$_{MD}$™) monitoring device.
- Battery fire containment assessment.

NAVAL RESEARCH LABORATORY: U.S. NAVAL RESEARCH LABORATORY

PREVENT: Develop Internal Short Circuit Triggers

Technology Gap identified in UN Manual of Testing and Criteria (UN 38.3) currently employed by DOT for technical risk analysis.





http://www.espec.co.jp/english/products/trustee/test/nail.html

RESEARCH NEED

Prevent future incidents through improved testing & validation methods which closely mirror failures in the field.

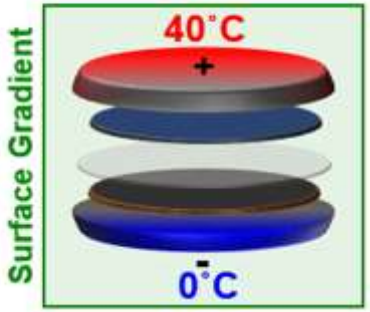
TECHNOLOGY GAP

Discover "trigger mechanisms" with the capability to form internal short circuits on demand.

RESEARCH OPPORTUNITY

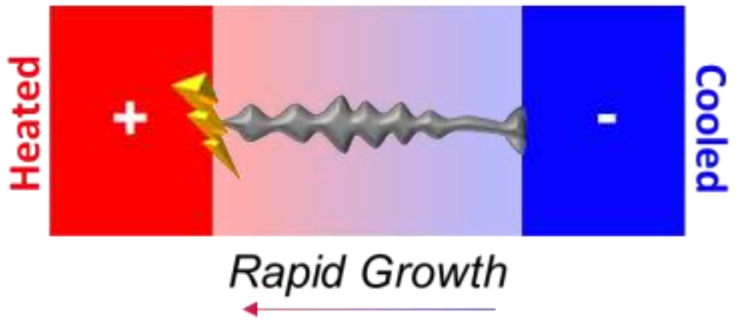
Develop advanced materials or methods to remediate lithium dendrite formation & growth leading to runaway.

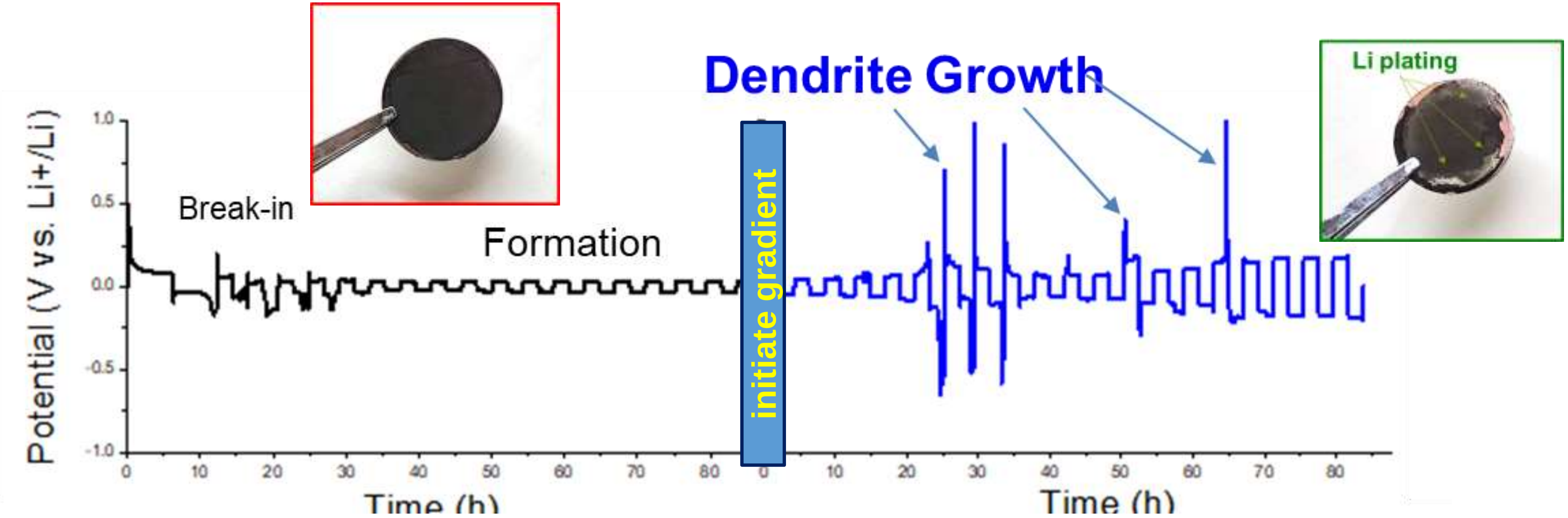
PREVENT: Develop Internal Short Circuit Triggers



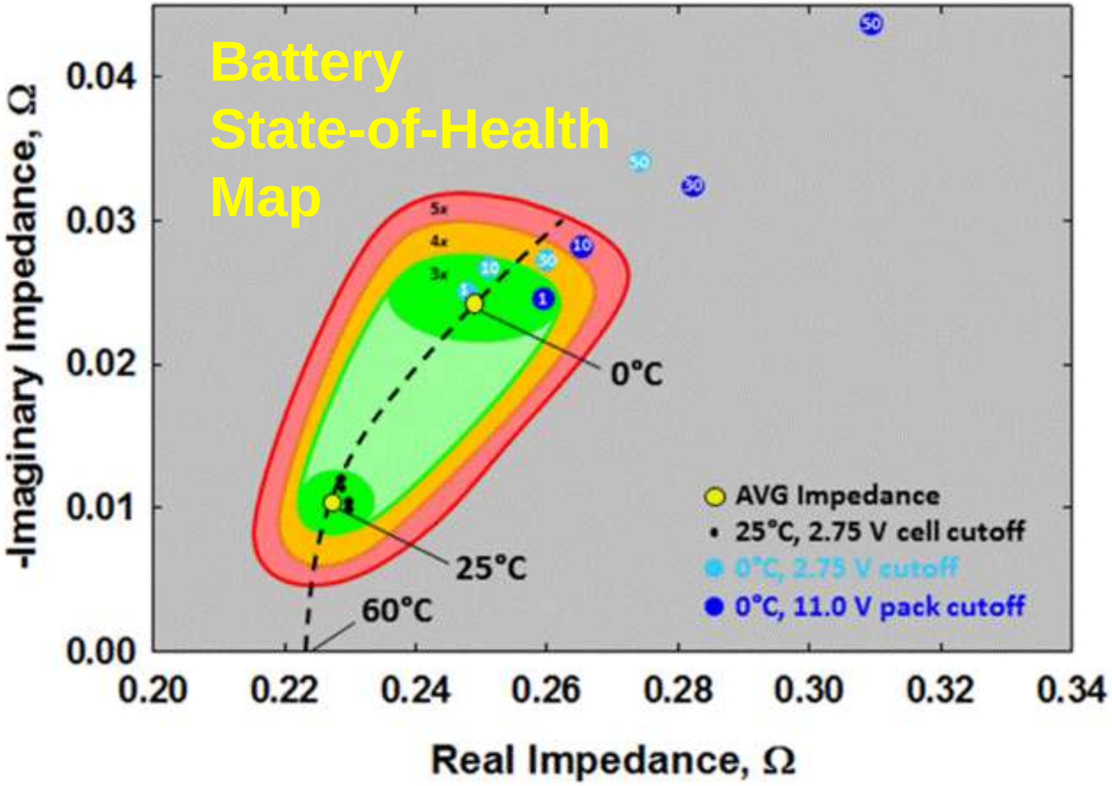
As received Li-ion Battery

Failure ***Initiated*** with Thermal Gradient





MITIGATE: Early Detection of Battery Instability



C.T. Love, M. Dubarry, T. Reshetenko, A. Devie, N. Spinner, K.E. Swider-Lyons and R. Rocheleau, "Lithium-Ion Cell Fault Detection by Single-Point Impedance Diagnostic and Degradation Mechanism Validation for Series-Wired Batteries Cycled at 0 °C," *Energies* **2018**, *11*, 834 **INVITED PAPER.**

RESEARCH NEED

Prevent future incidents through early warning, screening and fault detection methods.

TECHNOLOGY GAP

Identify unique indicators or "signatures" of inferior or comprised cells BEFORE failure.

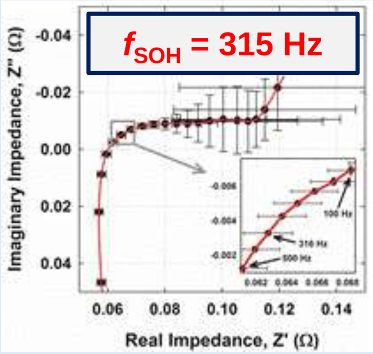
RESEARCH OPPORTUNITY

Develop diagnostic devices to generate hazard maps with primary scores for safety, stability and survivability.

MITIGATE: Early Detection of Battery Instability

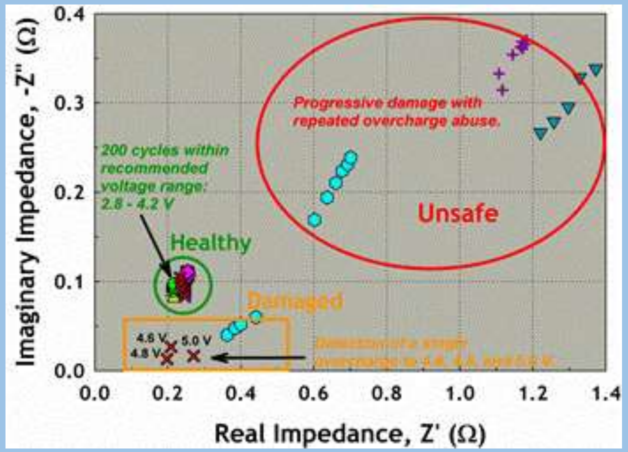
U.S. NAVAL RESEARCH LABORATORY

Observed Phenomena:

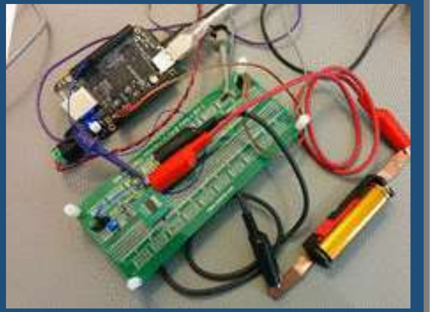


"Battery Health Monitoring System & Method"
US Patent No. 9,465,077

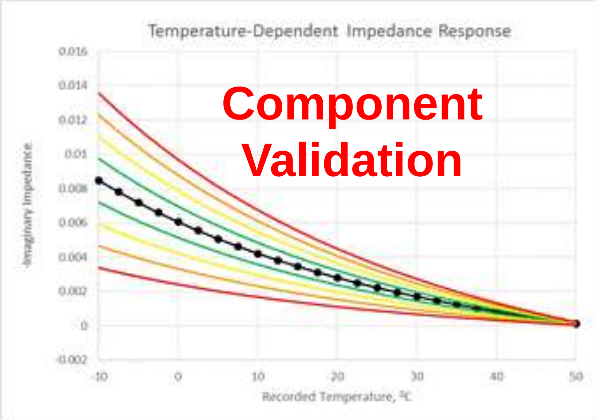
Demonstrated Use in Practice:

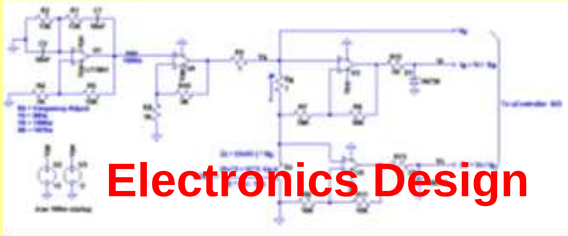


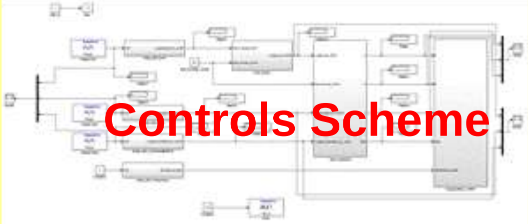
Breadboard Mock Up:



Hardware Design, Build and Prototype Development:







CONTAINMENT: Battery Failure and Fire Testing

RESEARCH NEED

Contain single failure events to eliminate cascading failures through entire battery packs or shipments.

TECHNOLOGY GAP

Non-propagating packaging schemes to contain single-cell failure and withstand impact.

RESEARCH OPPORTUNITY

Multi-layer laminates consisting of: thermal heat sink interior layer, high temperature, fireproof insulation core and impact resistant outer layer.

CONTAINMENT: Battery Failure via Accelerated Rate Calorimetry

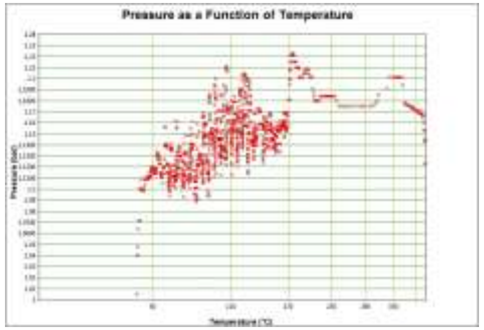
thermal hazard technology

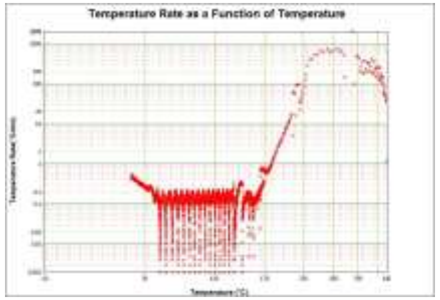
Successful installation and calibration of ARC instrument, ready to serve DOT researchers.

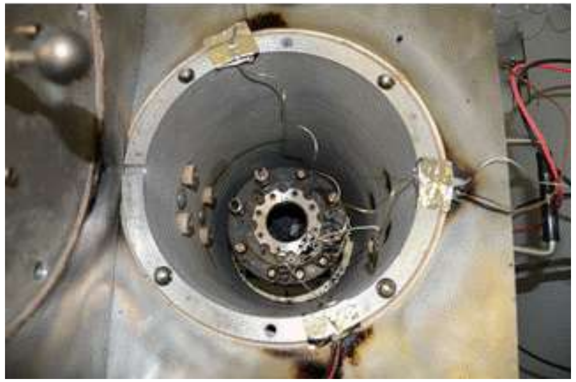
Capabilities:

EV calorimeter assembly:
25 cm dia. x 50 cm depth
temperature sensitivity:
0.02°/min
temperature range:
ambient to 400°C
8 thermocouples for multipoint analysis
heat capacity measurement unit
automated gas sampling at defined temperature
battery pressure kit" 4-liter capacity, 4 bar pressure

Ability to monitor temperature and pressure before and during thermal runaway events







CONTAINMENT: Defective Battery Fire Testing

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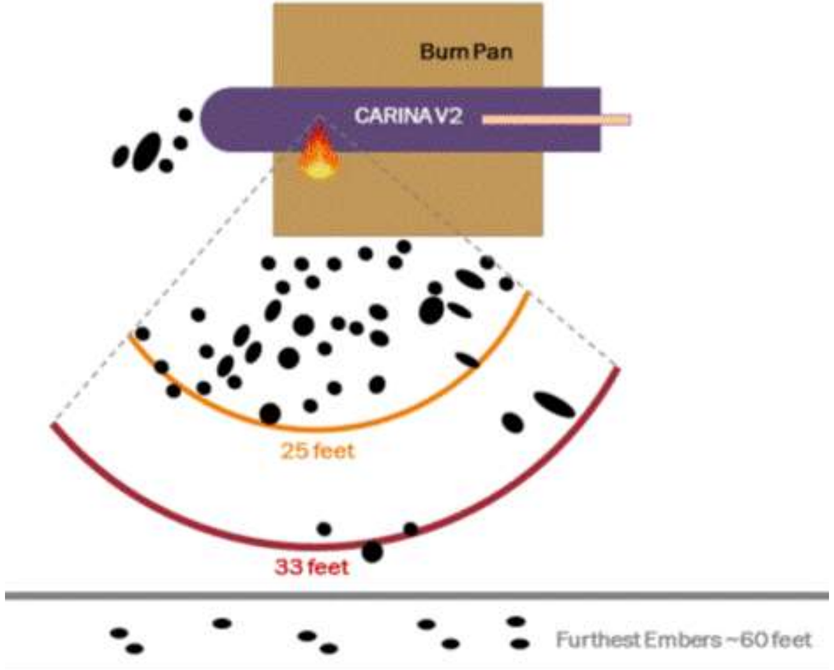

CONTAINMENT: Defective Battery Fire Testing

- Aerogel blanket performed well to maintain thermal and fire barrier
- Cell ejecta created small pinholes and tears in blanket
- Mechanical stiffening is required in future applications
- Chemical vapor detector could have prevented original failure due to electrolyte leakage
- Storage of combustible materials near large format batteries
- Use of fire extinguisher likely slows the propagation of fire but does not stop it
- Best fire fighting practices
- Refrigerated transportation is an effective means to reduce risk for transporting damaged batteries

Summary of Research Efforts, Fy16-18

- Internal short circuit triggering mechanism has been identified and is being refined. Temperature boundaries will be narrowed this FY and optimal ΔT recommended.
- Battery monitoring device (**Bat**$_{MD}$™) monitoring device. Development is ongoing and will be available to NSWC-Carderock for testing later this year.
- Fire containment material was assessed in simulated defective battery fire. More studies will be conducted this FY with improvements in mechanical properties to resist tearing and rupture.

Thank you!

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