

U.S. DEPARTMENT OF

Battery and Fuel Cell R&D

Vincent Sprenkle Technical Group Manager Electrochemical Materials and Systems Group Energy and Environment Directorate

DISCOVERY



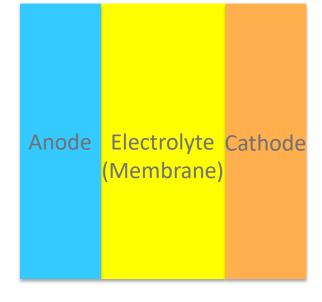
Outline

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- Basics of Fuel Cells and Batteries.
- Overview of Federal Program involving Batteries and Fuel Cells
- PNNL Development Efforts supporting these programs.



Basic Electrochemical Cell



Basic Electrochemical Cell – Fuel Cell

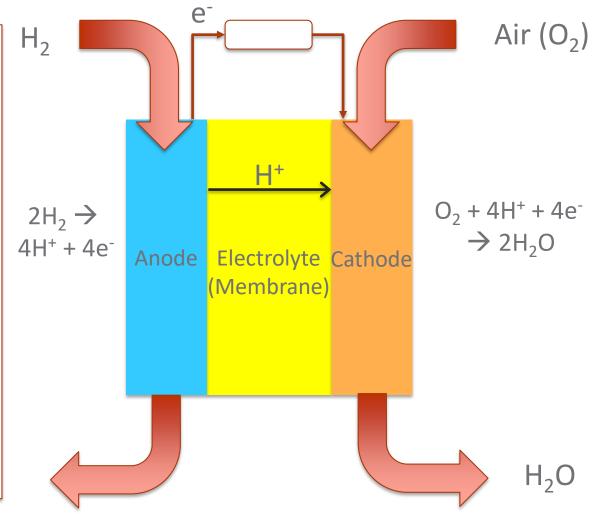


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Advantages

- No Combustion = High Efficiency
 - 2-3X ICE
- Not energy limited like batteries
- H₂O and Heat as byproducts (PEM)
- Repeat unit Voltage governed by Nernst Equation

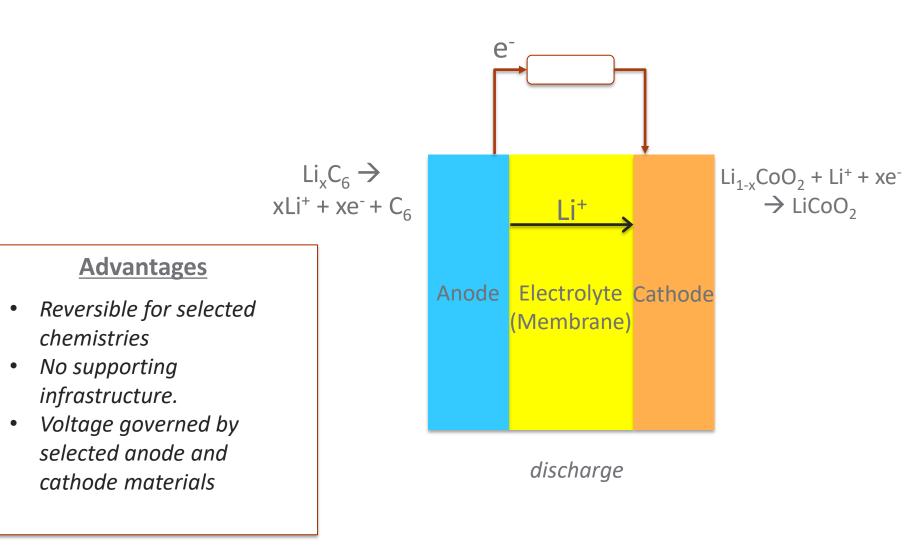
$$E = E^{0} + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]}$$



Basic Electrochemical Cell – Battery



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iPhone battery



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IPhone 6:	Anodes	Chemistry	Specific Capacity	Potential vs. Li⁺/Li
 1.80Ah 		Soft Carbon	< 700	~0
		Hard Carbon	600	~0
0.0 1011		Li ₄ Ti ₅ O ₁₂	175 / 170	1.55
 Voltage 3.81 Volts 		TiO ₂	168 / 168	1.85
		SnO ₂	782 / 780	< 0.5
	\neg	Sn	993 / 990	< 0.5
		Si	4198 / < 3500	0.5 ~ 1
Li-ion PolymerRattery 3 BZV===6 SHWhr ANN-6 616-0005 Anthorized Service		Chemistry	Specific Capacity	Potential vs. Li ⁺ /Li
Provider Only Potential for fire on burning. De not		LiCoO ₂	273 / 160	3.9
disassemble, puncture, crush, heat, or Bum		LiNiO ₂	274 / 180	3.6
15 227 204		LiNi _x Co _y Mn _z O ₂	~ 270 / 150~180	3.8
c Al üs		LiNi _x Co _y Al _z O ₂	~ 250 / 180	3.7
e		LiMn ₂ O ₄	148 / 130	4.1
		LiMn _{1.5} Ni _{0.5} O ₄	146 / 130	4.7
		LiFePO ₄	170 / 160	3.45
Li-ion		LiMnPO ₄	171 / 80~150	4.1
	Cathodes	LiNiPO ₄	166 / -	5.1
	cutioues	LiCoPO ₄	166 / 60~130	4.8



DOE Energy Storage and Fuel Cell Programs Goals and Objectives

Relevant DOE Programs for Battery and Fuel Cell Development Goals.



Fuel Cells

EERE – Hydrogen and Fuel Cell Office

2020 target to reduce PEM Fuel Cell costs to \$40/kW and H₂ production to <\$4/gge

FE – Solid Oxide Fuel Cell Program

• Demonstrate MW scale SOFC system operating > 50% efficiency.

ARPA-e - RANGE/REFUEL, etc.

Varies by project.

Battery

EERE – Vehicle Technologies Program

- Increase EV range to 300 miles and decrease charge time to 15 minutes or less at \$80/kWh pack.
- Battery 500 2-3X increase in energy density over today's Li-ion
- SC Joint Center Energy Storage Research (JCESR)
 - 5-5-5: Materials and systems at 5X higher performance and 5X lower cost.

OE – Grid Scale Energy Storage

 Improve Reliability and Safety, cost proposition, regulatory treatment, and industrial acceptance of grid scale energy storage. Target < \$125/kWh

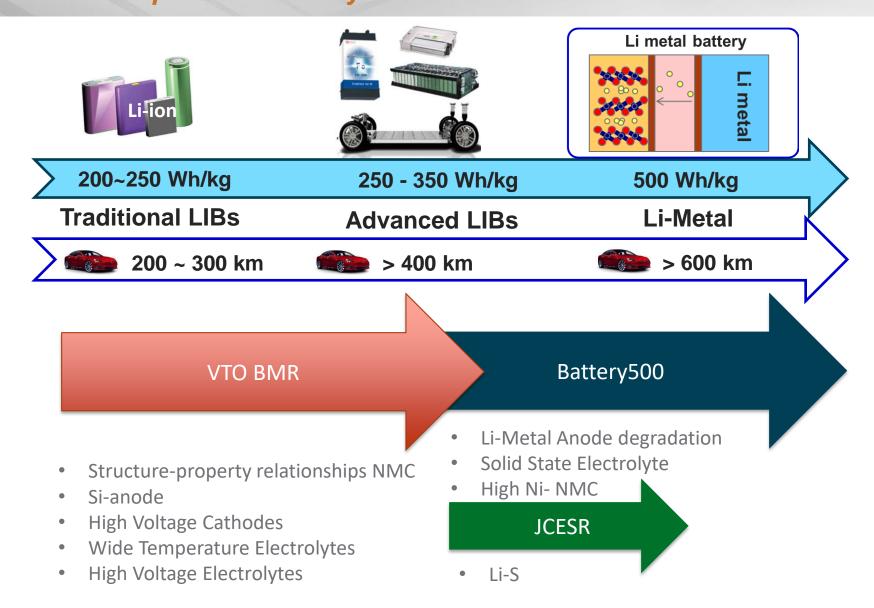
ARPA-e – multiple programs

• Varies by project, overall \$100/kWh cost target.

Transportation Energy Storage Roadmap *Moving to Li-metal based batteries will require increased emphasis on safety*.



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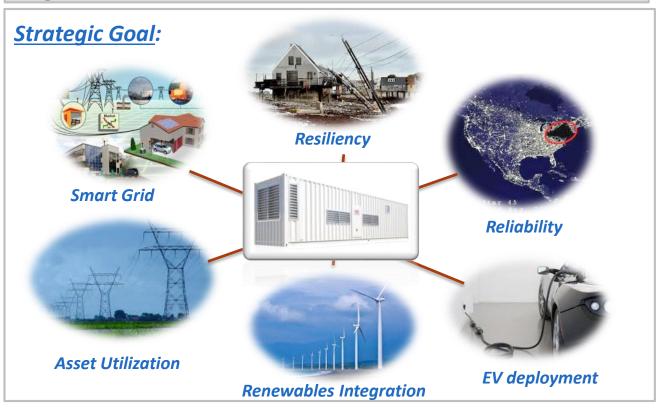


DOE OE Energy Storage Program

Challenges:

- Cost competitive energy storage technologies
 - Targeted scientific investigations of key materials and systems
- Validated reliability & safety
 - Independent testing of prototypic devices and understanding of degradation.
- Equitable regulatory environment
 - Enable Industry, Utility, Developer collaborations to quantify benefits provide input to regulators.
- Industry acceptance
 - Highly leverage field demonstrations and development of storage system design tools

Mission: To enable energy storage to provide multiple benefits for critical grid applications, DOE is accelerating adoption of energy storage through: improving the technology, field demonstrations, and innovative market design.



PNNL – OE Energy Storage Program Activities that support these Challenges



Supporting WA and OR dockets on ESS

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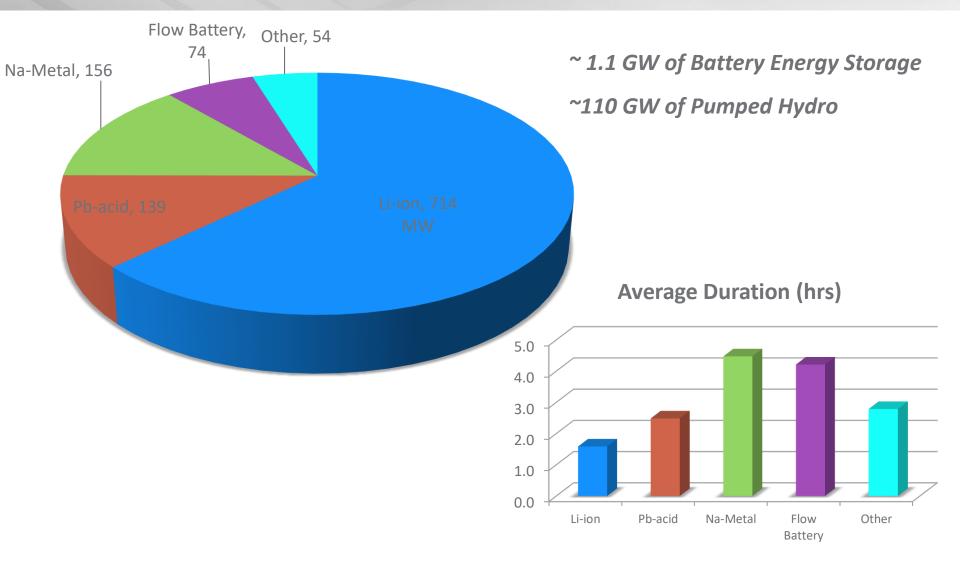


Offers potential for longer cycle-life and lower cost.

Current Grid ESS deployments (Battery Only)



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Source: DOE Global Energy Storage Database http://www.energystorageexchange.org/



Safety Related Issues with ESS Technologies

Li-ion: Basic Electrochemical Reaction



Specific Potential Potential Chemistry **Specific Capacity** Chemistry Capacity vs. Li⁺/Li vs. Li⁺/Li LiCoO₂ 273 / 160 3.9 Soft Carbon < 700 < 1 Hard Carbon 600 LiNiO₂ 274 / 180 3.6 < 1 ~ 270 / 175 / 170 $Li_4Ti_5O_{12}$ 1.55 3.8 LiNi_xCo_yMn₂O₂ Positiv 150~180 TiO₂ 168 / 168 1.85 (Li, Host LiNi, Co, Al, O, ~ 250 / 180 3.7 SnO₂ 782 / 780 < 0.5 LiMn₂O₄ 148 / 130 4.1 Sn 993 / 990 < 0.5 146 / 130 LiMn_{1.5}Ni_{0.5}O₄ 4.7 4198 / < 3500 Si $0.5 \sim 1$ **LiFePO**₄ 170 / 160 3.45 Non-aqueous e-1 e-1 Liquid Electrolyte 171 / LiMnPO₄ 4.1 80~150 LiNiPO₄ 166 / -5.1 166 / LiCoPO₄ 4.8 60~130 Current Current Collector Collector $Li_{1-x}CoO_2 + xLi^+ + xe^- \xrightarrow{discharge} LiCoO_2$ Cathode: $Li_{x}C_{6} \xrightarrow{discharge} xLi^{+} + xe^{-} + C_{6}$ Anode: Full Cell Reaction: $LiC_6 + CoO_2 \xrightarrow{discharge} C_6 + LiCoO_2 \quad E = 3.7V \text{ at } 25^\circ C$

Source: Z. Yang JOM September 2010, Volume 62, Issue 9, pp 14-23



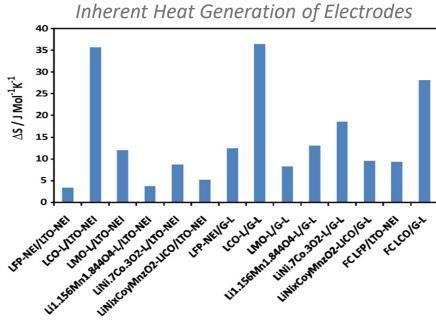
Li-ion Safety Issues

High Temperature

- Typical operating window 0-50° C
- Operation above this temperature can lead to organic electrolyte decomposition and flammable gas generation.

Overcharging

Max voltage depends on materials, overcharging can lead to Li metal plating on anode, potential for short



Mechanical Impact

■ Can create internal short, leading to elevated temperature during operation.

Internal shorts

Manufacturing defects and or dendrite growth from overcharging leads to increased temperature during operation.

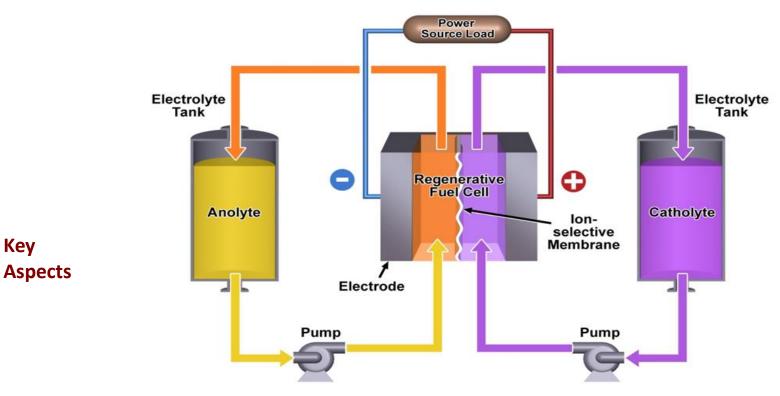
All events can lead to thermal runaway.

Severity of runaway depends on: Amount of stored energy (SOC), battery materials, and design of cells/pack.



- Power and Energy are separate enabling greater flexibility and safety.
- Suitable for wide range of applications 10's MW to ~ 5 kw
- Wide range of chemistries available.
- Low energy density ~ 30 Whr/kg \geq

Key



Redox Flow Batteries -Advantages/Issues



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Temperature

- High/Low Temperatures can lead to precipitation of species
- Typical range -10-60° C

Charging

Overcharging can lead to evolution of hydrogen (H₂O electrolysis)

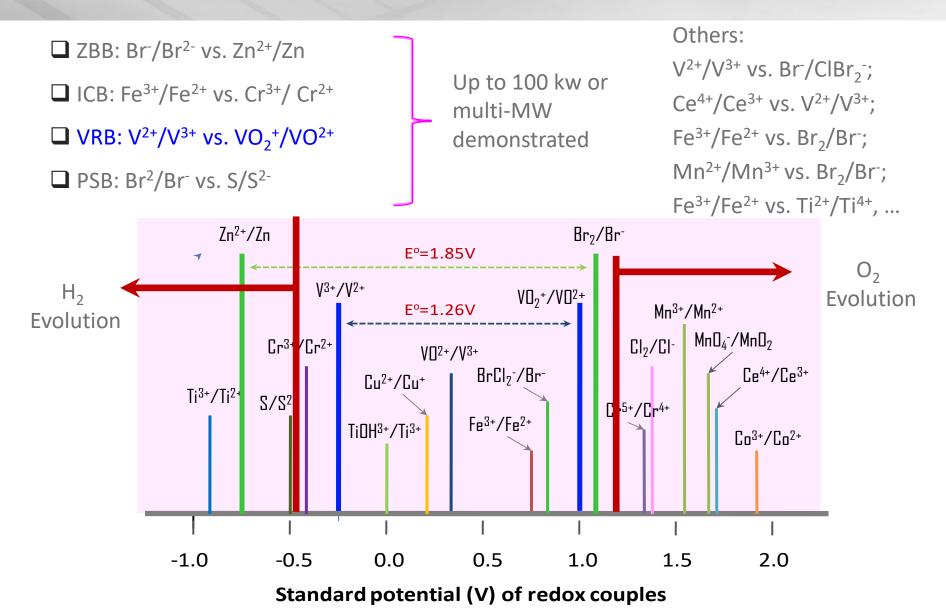
Toxicity of Elements

- Solutions are in pumped system, susceptible to leaks.
- Minimal Fire Hazard
 - Electroactive element in aqueous solution
- High Degree of Flexibility

Redox Flow chemistries

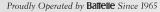


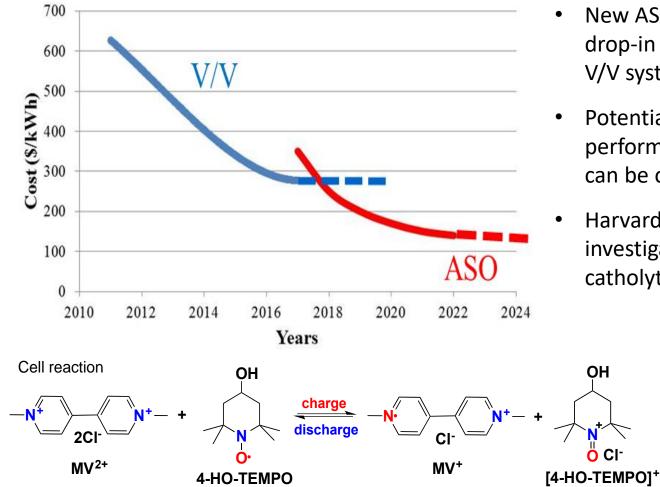
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Cost Competitive Technologies Redox Flow Battery







- New ASO being designed as drop-in replacement to current V/V systems.
- Potential for ½ cost reduction if performance and stability targets can be obtained.
- Harvard, Case Western investigating alternate catholytes.

Advanced Energy Materials 6(3):1-8 (Dec. 2015)



Sodium β"-Alumina Batteries (NBBs)

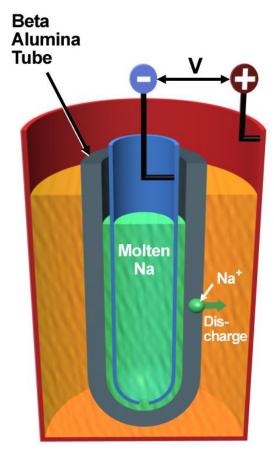
- Batteries consisting of *molten sodium anode* and $\beta''-Al_2O_3$ solid *electrolyte* (BASE).
 - Use of low-cost, abundant sodium \rightarrow low cost
 - High specific energy density (120~240 Wh/kg)
 - Good specific power (150-230 W/kg)
 - Good candidate as a large-scale energy storage
 Device for renewable energy
 - Operated at relatively high temperature (300~350°C)

Sodium-sulfur (Na-S) battery

- 2Na + xS \rightarrow Na₂S_x (x = 3~5)
 - E = 2.08~1.78 V at 350°C

Sodium-nickel chloride (Zebra) battery

- 2Na + NiCl₂ \rightarrow 2NaCl + Ni
 - E = 2.58V at 300°C
 - Use of catholyte (NaAlCl₄)





Na-metal Safety Issues

Temperature

- No high temperature concern, typical operating window 200-350° C
- At < 98° C, Na metal freezes out, degree of distortion to cell dictated by SOC of battery (amount of Na in anode)

Charging

<u>Na-Metal Halide</u>: Voltage Range 2.8V – 1.7 V. > 2.8 V lead to melt degradation and increased resistance, < 1.7 V leads to Al plating</p>

Mechanical Impact

- Solid ceramic electrolyte keeps reactive elements from contact. Failure in electrolyte can lead to exothermic reaction (Na-S)
 - <u>Na-Metal Halide</u>: Secondary electrolyte (NaAlCl₄) decomposes in contact with Na metal to form Al, helps blunt propagation of reaction.
- If severe enough impact, Na metal can escape cell and react with 0₂, H₂0 and/or form short (NGK- Tsukuba Plant)



Lead-acid battery Asymmetrical capacitor Separator Separator **Negative plate reaction:** PbO: PbO₂ Capacitor electrod • Pb(s) + HSO⁻₄(aq) Responding to Responding to \rightarrow PbSO₄(s) + H⁺(aq) + 2e⁻ energy requirements pulse power requirements **Positive plate reaction:** $PbO_{2}(s) + HSO^{-}_{4}(aq) + 3H^{+}(aq) + 2e^{-}$ \rightarrow PbSO₄(s) + 2H₂O(I) Separator UltraBattery Capacito PbO, electrod The total reaction can be written as $Pb(s) + PbO_2(s) + 2H2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

OCV = 1.95 (fully discharged) ~ 2.10 (fully charged) V at RT

Technical Challenges/Drawbacks

- Limited life time (5~15 yrs)/cycle life (500~1000 cycles) and degradation w/ deep discharge (>50% DoD)
- Low specific energy (30-50 Wh/kg)
- Environmental concerns

Lead-Acid Battery



Pb-acid Safety Issues

Acid/Corrosion

- Sulfuric acid solution
- Sulfation by storing for prolonged periods for extended time leads to permanent failure – may increase overpotential during charge, leading to gassing.

Temperature

Precise float voltage required to adjust for temperature effects or can go into overcharging condition

Charging

- Overcharging can lead to evolution of hydrogen (H₂O electrolysis)
- Explosion if not design correctly.
- Active material shedding may cause internal shorts if not designed properly

Toxicity of Elements

- Environmental concerns for Pb, largely recyclable.
- Commonality
 - Because people use Pb-acid on daily basis, people believe they can work with them.



DOE OE Efforts to Improve Safety and Reliability of Energy Storage Systems

ESS Safety and Reliability DOE Reliability Workshop



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- Identify key challenges and opportunities facing the reliable operation and deployment of energy storage.
- Key Outcomes/Needs
 - Reliability testing on deployed systems with consistent standards.
 - 2. Data sharing across industry to accelerate deployment.
 - 3. Develop the scientific understanding and technical basis for reliable operation



DOE ESS Reliability Workshop June 14-15, 2016 - Kennewick, WA



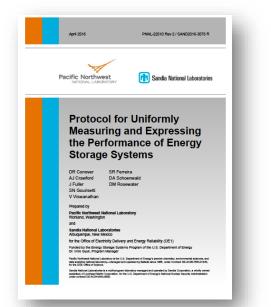


ESS Safety and Reliability Safety and Performance Documents



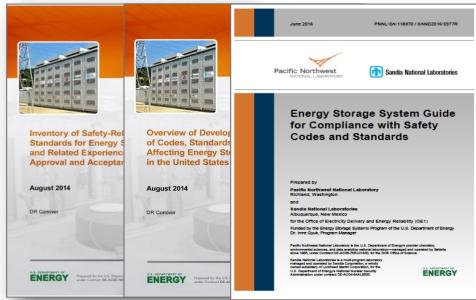
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Performance Protocol -Rev 2 released April – 2016



Protocol for Uniformly Measuring and Expressing the Performance of Energy Storage Systems, PNNL-22010 Rev 2 / SAND2016-3078R

Storage Safety Codes and Standards



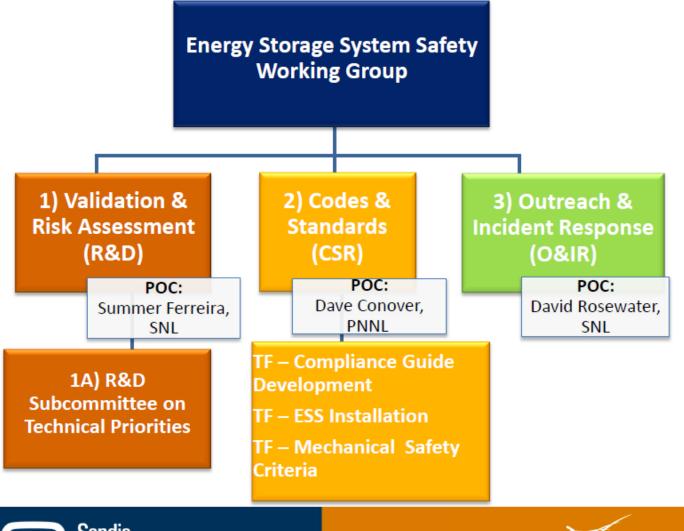
 Inventory of Safety-related Codes and Standards for Energy Storage Systems with some Experiences related to Approval and Acceptance 2014. PNNL-23618,
 Overview of Development and Deployment of Codes, Standards and Regulations Affecting Energy Storage System Safety in the United States - Conover DR. 2014. PNNL-23578,

3.) Energy Storage System Guide for Compliance with Safety Codes and Standards. 2016. PNNL-SA-118870





Energy Storage Safety Working Group Organizational Structure







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Documenting and Verifying the Safety of Energy Storage Systems through Codes and Standards







Pam Cole Dave Conover Pacific Northwest National Laboratory DOE OE Energy Storage Peer Review Washington, DC September 27, 2016

Purpose and Expected Outcomes

Purpose - to emphasize the value of focusing on safety related codes and standards (CS) to successful ESS deployment (or why didn't I get involved with CS sooner because I am behind the 8-ball)

Expected Outcomes

- Recognition that while codes and standards can facilitate technology acceptance they can also adversely impact technology deployment
- A better understanding of key codes and standards affecting energy storage systems (ESS) and how they are developed and deployed
- Familiarity with the processes associated with documenting and verifying the acceptability of ESS in relation to the criteria in codes and standards
- A desire to collaborate with others and increase involvement in codes/standards development in order to support more uniform, timely and easier deployment of safe ESS





Summary of DOE OE ES Safety Efforts



- Strategic Plan developed, being implemented and evolving to respond to technology and safety needs
- Engaging a wide range of organizations and entities to foster increased cooperation and collaboration on safety
- Ensure research needed to address safety questions and issues is identified, conducted and coordinated and the results available for application in the development and deployment of safe ESS
- Facilitate acceptance of ESS through codes and standards
- Develop new and update existing codes and standards to provide appropriate criteria to guide the development and deployment of safe ESS
- Ensure everyone involved in the development and deployment of ESS have information necessary to perform their role in ensuring ESS safety
- Evolve and 're-boot' as we learn more and ESS technology changes

Grid Energy Storage Safety



December 2013

"Facilitating the timely development and deployment of safe ESS by implementing the DOE ESS Safety Plan through collaboration of all interested parties and key stakeholders"





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Safety-Related Issues in Codes and Standards

- ESS 'product' configuration and how safety of the ESS is validated
- New versus existing systems and new versus existing building/facility applications
- Siting (location, loads, protection, egress/access, maximum quantities of chemicals, separation, etc.)
- Ventilation, thermal management, exhausts (when necessary, flow rates, how controlled, etc.)
- Interconnection with other systems (energy sources, communications, controls, etc.)
- Fire protection (detection, suppression, containment, smoke removal, etc.)
- Containment of fluids (from the ESS and from incident response)
- Signage and markings





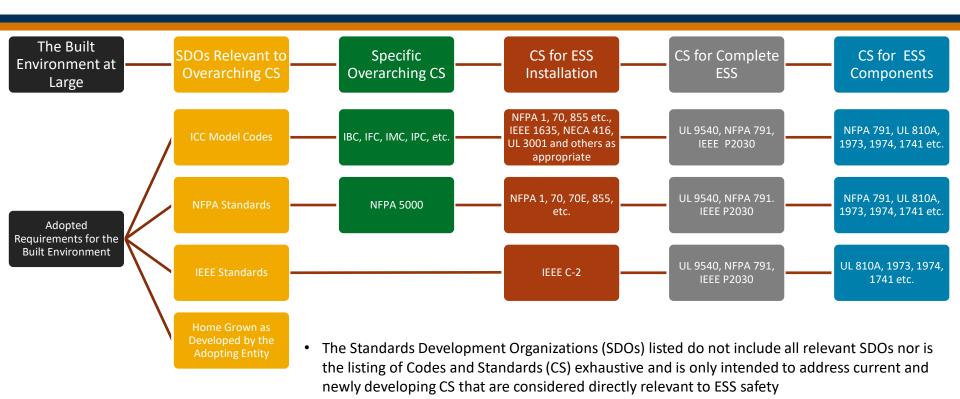
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Factors that Affect the Critical Nature of an Issue

- ES technology type
- Chemistry of any batteries
- Location in relation to the built environment and public
- Size/capacity
- Anticipated natural and man made influences



Codes and Standards Hierarchy for ESS



- The information reads from left (macro level) to right (micro level) covering the built environment at large, then a more specific focus on entire buildings and facilities, then the installation of an ESS, then the ESS as a complete product and finally the components (parts) of the ESS product what is left is intended to be considered the 'parent' to what is immediately to the right
- The CS covered are developed in the voluntary sector by SDOs those who adopt those documents (in total or in part) or who adapt them
 and develop their own 'home grown' provisions include Federal, state, local, territorial and tribal agencies as well as certain regulated
 utilities such as communications providers (on the customer side of the meter) and regulated utilities on the grid side of the meter





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Criteria to Address Safety – ESS Components and Entire Systems

CS for ESS Components

Test and list the component to document and validate it complies with the relevant standard

- > UL 489 (Circuit Breakers)
- UL 810A (Electrochemical Capacitors)
- > UL 1642 (Lithium Batteries)
- UL 1741 (Inverters)
- UL 1973 (Batteries for Stationary Applications)
- > UL 1974 (Second Use Batteries)
- UL 791 (Evaluation of unlisted electrical equipment)

CS for Complete ESS

Test and list the system to document and validate it complies with the relevant standard

- UL 9540 (Safety for ESS)
- UL 3001 (Safety for Distributed Energy Generation and ESS)
- > ASME TES-1 (Molten Salt Thermal Energy Storage Systems)
- UL 791 (Evaluation of unlisted electrical equipment)





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Example CSR Engagement: NFPA

N	FPA[®]

	National Fire Protection Association (NFPA)—www.nfpa.org
Document:	NFPA 1-18 Fire Code
ESS relevance:	Chapter 52 includes requirements related to ESS.
Previous activity:	Finalization of the 2018 edition through the NFPA standards development process at the NFPA Technical Meeting in June 2017 (subject to an appeal to and consideration of the appeal by the NFPA Standards Council subsequent to the technical meeting).
Current activity:	After the 2018 edition is published, public inputs for the 2021 edition will likely be due in July 2018.
Date of next edition:	2021
Document:	NFPA 70-17 National Electrical Code
ESS relevance:	Article 706 (new) applies to energy storage systems and Article 480 applies to batteries, in addition to other criteria in the NEC relevant to electrical equipment and installations.
Previous activity:	Development by the DC task group (under NFPA) of a new Article 706 covering energy storage systems and its inclusion in the 2017 edition of the NEC. An NEC task group has completed a draft of materials intended to align Articles 480 (batteries) and 706.
Current activity:	A preliminary review of the draft materials aligning Articles 480 and 706 has been completed by members of the DC task group. It is anticipated that the work of the DC task group moving forward will dovetail into the NEC task group aligning Articles 480 and 706. Proposed changes to the NEC are due September 7, 2017.
Date of next edition:	2020
Document:	NFPA 5000-18 Building Code
ESS relevance:	Provides a basis for adoption and application of other standards.
Previous activity:	Finalization of the 2018 edition through the NFPA standards development process at the NFPA Technical Meeting in June 2017 (subject to an appeal to and consideration of the appeal by the NFPA Standards Council subsequent to the technical meeting).
Current activity:	After the 2018 edition is published public inputs for the 2021 edition will likely be due in July 2018.
Date of next edition:	2021





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Example CSR Engagement: IEEE

	IEEE—www.ieee.org	
Advancing Technology	http://standards.ieee.org/about/nesc/	
for Humanity	C2-17 National Electric Safety Code	
ESS relevance:	Covers electrical safety for utility systems and equipment.	
Previous activity:	Completion and publication of the 2017 edition of the NESC.	
Current activity:	Final date to receive change proposals from the public for revision of the 2017 edition leading to the 2022 edition is July 15, 2018. Change proposals will then be compiled and NESC Subcommittees then consider those proposals and prepare their recommendations in September/October of 2018. Preprint of the changes proposals available and open for public comment on September 1, 2019.	
Date of next edition:	August 1, 2021	
Activity:	IEEE Energy Storage and Stationary Battery Committee (ESSB)	
ESS relevance:	This is a growing subcommittee of the power and energy society that manages many of the standards around energy storage and battery technologies. <u>http://sites.ieee.org/pes-essb/</u>	
Previous activity:	Meeting held June 2017.	
Current activity:	The Next meeting is in Jacksonville Florida, January 22, 2018 - January 25, 2018.	
Date of next edition:	N/A	





Example of Involvement in CS – ICC IFC and NFPA 855

CS for ESS Installation

▹ ICC IFC

- Code change proposal F95-16 by the ICC Fire Code Action Committee (FCAC) revises Section 608 on stationary battery storage systems to address more than the current code (lead acid)
- Input to the proposal provided under the ESS Safety Plan
- The proposal was approved as modified at the public hearings (April 2016)
- Public Comments have been submitted by the FCAC to enhance the proposal editorially and technically based on comments provided during the public hearings and subsequent work by an energy storage task group under the FCAC

> NFPA 855

- Draft pre-standard finalized based on input from the single standard task force of the CSR WG under the ESS Safety Plan and the document forwarded to NFPA
- NFPA filed a Project Initiation Notification (PINS) with ANSI for such a standard and voted to establish a new committee to draft a standard (855) in April 2015
- The NFPA Standards Council has appointed the members of the new technical committee (TC) and those members were notified in late August
- The TC is now charged with development of the official scope for the standard for presentation to the SC for approval





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Summary and Key Takeaways

- Energy storage technology includes more than just batteries and has a wide range of potential applications
- ✓ Current and future battery technology is a foundation for energy storage technology
- CS provide a basis for the safe installation, application and use of ESS
- CS lag technology development and need to be updated to address all ESS technologies and potential applications
- Current CS contain the basis for prescriptively documenting and evaluating safety of some batteries and some ESS
- Current CS contain the foundation for documenting and evaluating safety of all ESS based on equivalent safety via alternative methods and materials
- Until CS are updated and contain necessary and relevant prescriptive guidance documenting and validating the safety of an ESS is more likely to be on a case-bycase basis
- Collaboration on the enhancement of the compliance guide and updating of current CS to cover more ESS technologies and applications can foster more timely consideration and acceptance of ESS





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ESS Safety Related Resources

US. DEPARTMENT OF Energy Storage Systems Program

http://www.sandia.gov/ess/

Events/News Publications Tools Resources

Tools

The ESS Program continually documents progress in the world of energy storage. That progress takes many forms and comes from many sources.

ESS Program Tools

- DOE/EPRI 2015 Electricity Storage Handbook in Collaboration with NRECA The DOE/EPRI 2015 Electricity Storage Handbook in Collaboration with NRECA is a how-to guide for utility and rural cooperative engineers, planners, and decision makers to plan and implement energy storage projects.
- PUC Handbook A perspective on issues pertaining to the deployment of utility procured electrical energy storage resources. The intended audience includes state electric utility regulatory authorities, their staffs and the planning personnel in the utilities they regulate.
- DOE Global Energy Storage Database Free, up-to-date information on grid-connected energy storage projects and relevant state and federal policies. All information is vetted through a third-party verification process. All data can be exported to Excel or PDF.
- ES-Select ToolTM The ES-SelectTM Tool aims to improve the understanding of different electrical energy storage technologies and their feasibility for intended applications in a simple, visually comparative form. It treats the uncertainties in technical and financial parameters as statistical distributions.
- · Protocols A listing of DOE-published protocols for download.



ENERG	ing Storage By Systems Program Events/News P
	Publications
	The ESS Program continually documents progress in the world of grid energy storage. That progress takes many forms and comes from many sources: ESS Program Publications
	Journal Articles and Books Patents and Applications DOE Office of Electricity (DOE) Sandia National Laboratories (SNL) Pacific Northwest National Laboratory (PNNL) Oak Ridge National Laboratory (ORNL)
	Conference Archives DE Energy Storage Systems Peer Review Meetings EESAT Conferences
	Webinars • Energy Storage in State RPSs: State-Federal RPS Collaborative Webinar (PDF Slides, 5:25 MB) – December 19, 2011. Hosted by Clean Energy States Alliance. The webinar was web site.
	DOE/EPRI/NRECA DOE/EPRI 2015 Electricity Storage Handbook in Collaboration with NRECA
	NYSERDA/DOE Joint Initiative Publications (Scroll to "R&D Technical Reports—Electric Power Delivery")
	Factsheets - DOE - SNL
	R&D 100 Awards

Projects

Award

Dr. Imre Gyuk, DOE-Office of Electricity Delivery and Energy Reliability







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Summer Ferreira Chris LaFleur Alice Muna Dave Rosewater Sandia



Pam Cole Dave Conover PNNL







For more information on DOE OE ESS safety activities contact <u>energystorage@sandia.gov</u>

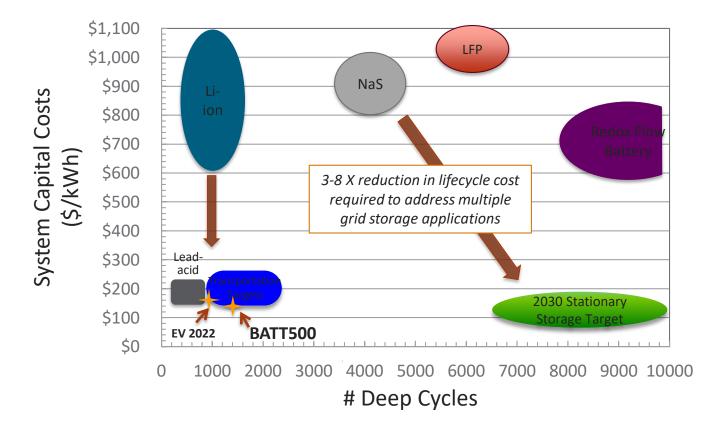
Dr. Imre Gyuk, DOE-Office of Electricity Delivery and Energy Reliability All the participants of the working groups

Energy Storage Technology: Future Challenges & Opportunities



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PNNL programs are at the center of both Transportation and Grid Energy Storage S&T challenges



Hission

We transform the world through courageous discovery and innovation.

PNNL science and technology inspires and enables the world to live prosperously, safely and securely.

DISCOVERY





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PV Smoothing

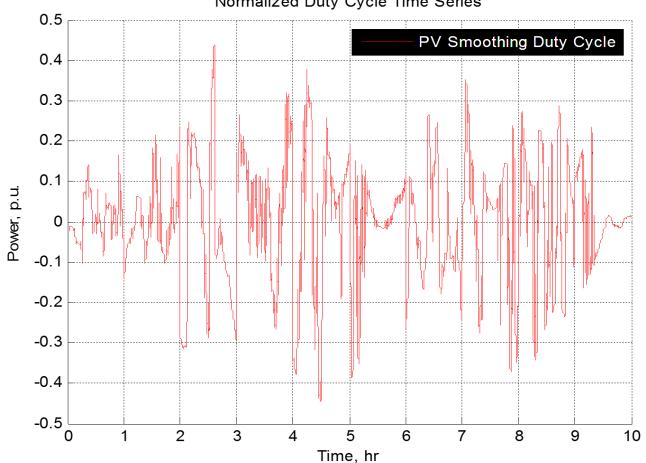


- ESS mitigates the rapid fluctuations in PV power output that occur during periods with transient shadows on the PV array by adding power to or subtracting power from the PV system output to smooth out the high frequency components of the PV power
- Reference performance metrics apply as they are 'blind' as to application and duty-cycle
- Duty-cycle performance metrics (Table 4.4.3(a.)) apply with tests for each run using the PV smoothing duty cycle

PV Smoothing Duty-Cycle



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Normalized Duty Cycle Time Series