Pacific Northwest
NATIONAL LABORATORY

Beyond-Lithium Batteries: From Human Intuition to Artificial Intelligence

Vijay Murugesan
Staff Scientist, Materials Sciences

We will begin shortly….

We value your feedback!

https://www.surveymonkey.com/r/PNNL042021

U.S. DEPARTMENT OF ENERGY BATTELLE
PNNL is operated by Battelle for the U.S. Department of Energy

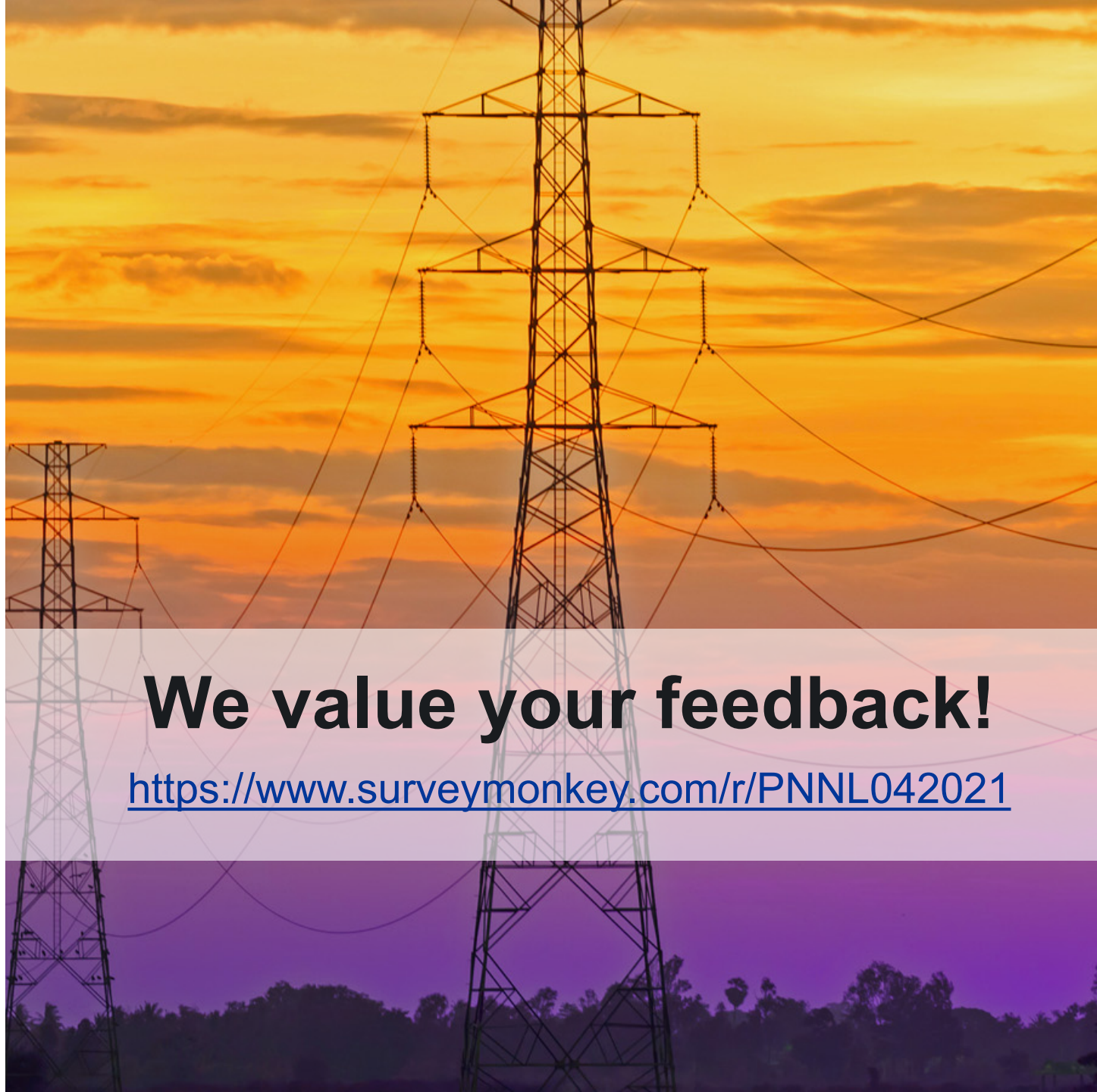
Pacific Northwest
NATIONAL LABORATORY

Beyond-Lithium Batteries: From Human Intuition to Artificial Intelligence

Vijay Murugesan
Staff Scientist, Materials Sciences

U.S. DEPARTMENT OF ENERGY BATTELLE

PNNL is operated by Battelle for the U.S. Department of Energy



We value your feedback!

https://www.surveymonkey.com/r/PNNL042021

Pacific Northwest
NATIONAL LABORATORY

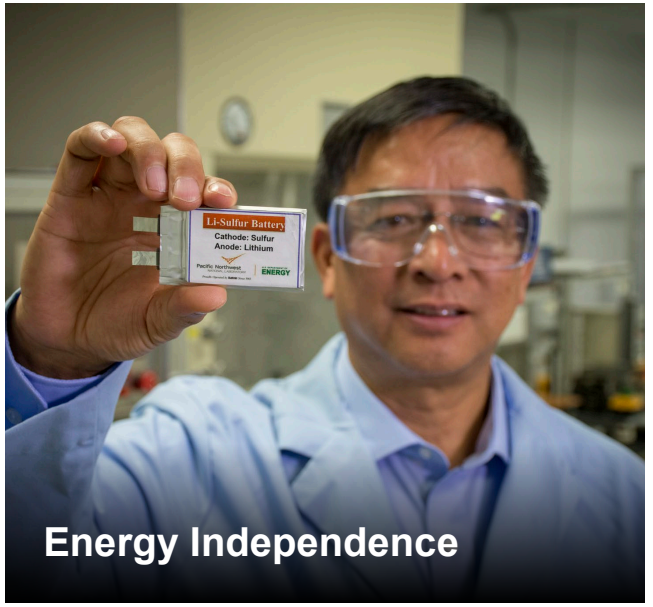
1 of 17

U.S. DOE Labs

Pacific Northwest
NATIONAL LABORATORY

PNNL is Focused on **DOE's MISSIONS** and Addressing Critical **NATIONAL NEEDS**

Scientific Discovery



Energy Independence


National Security

Environmental Management

Pacific Northwest
NATIONAL LABORATORY

PNNL is an ECONOMIC ENGINE

4,997
Employees

340
Inventions

$1.46B
Total Economic Output

$1.1B
Annual Spending

81
Patents

7,180
Jobs Generated
in Washington

$487M
Total Payroll

36
Licenses

198
Companies
with PNNL Roots

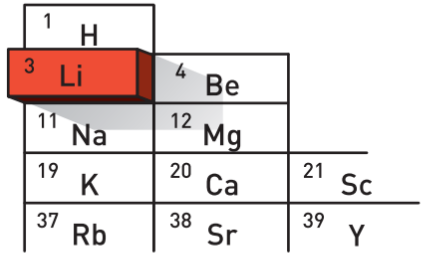
Pacific Northwest NATIONAL LABORATORY

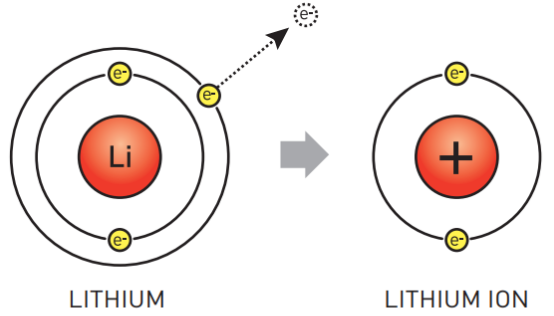
50+ Years

Developing Goodwill

Over the Years	**$29M**	**334,000**	**>120**
FY20	**$1.08M**	**5,660**	**56**
	Philanthropic Investments	Team Battelle Volunteer Hours	Community Organizations

Lithium (Li) – First Metal on Periodic Table





©Johan Jarnestad/The Royal Swedish Academy of Sciences

"Ein neues mineralisches Alkali und ein neues Metall (a new mineral alkaline and a new metal)"

-Johan August Arfwedson (1817)

"a shining, white, combustible metal"

-William Thomas Brande (1821)

"highest electrode potential" – i.e., Li is more electromotive than any other metal

-Lewis and Keyes (1913)

Journey to Lithium-Ion Battery

2019 Nobel Prize - Chemistry

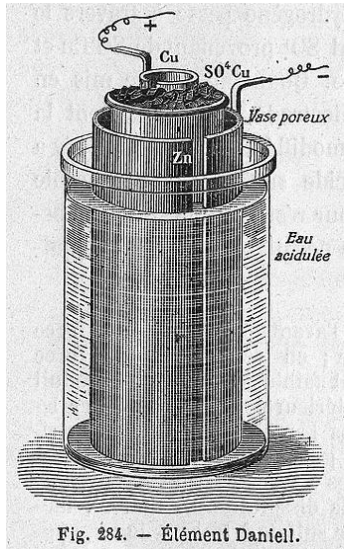
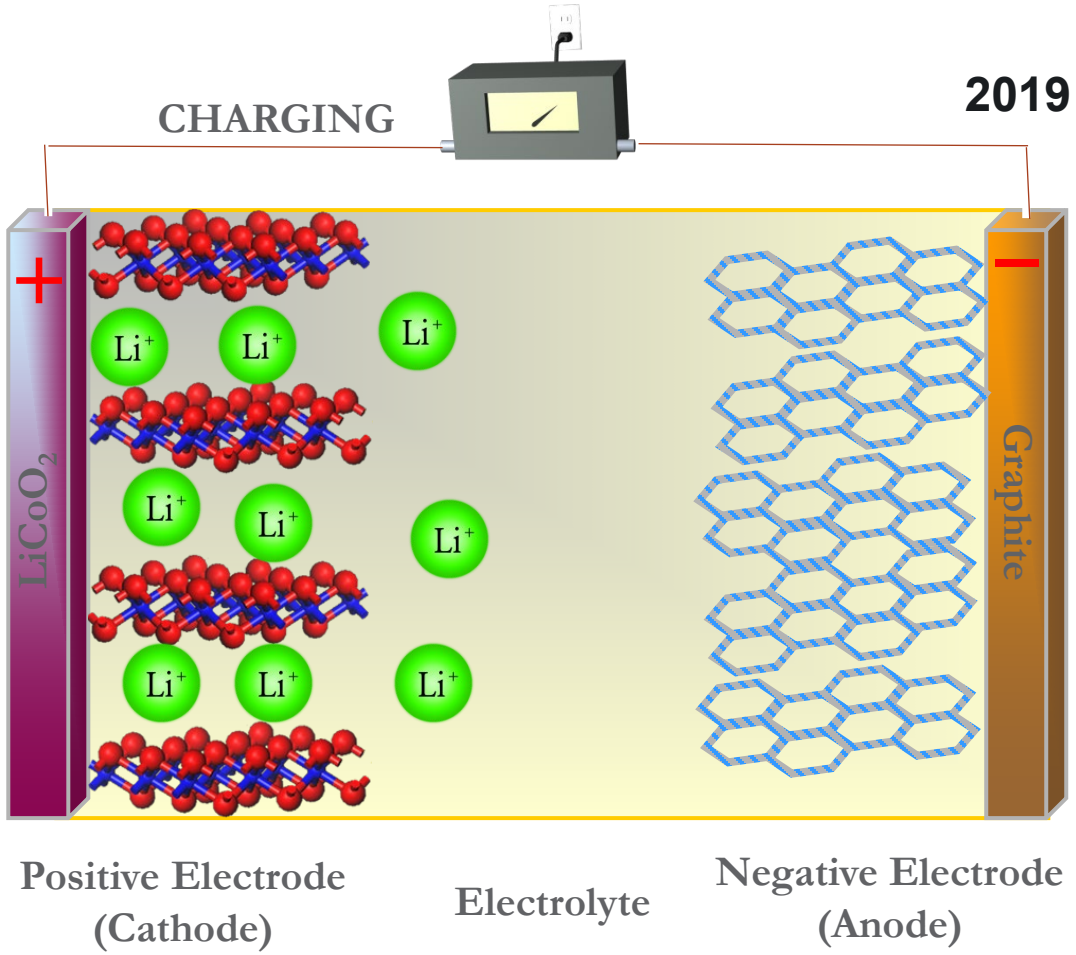
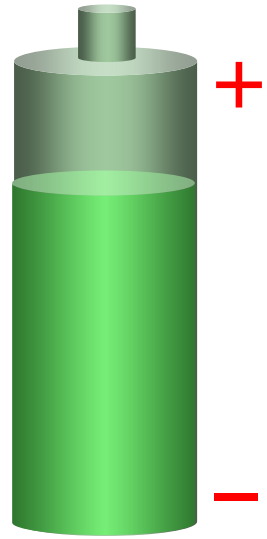


Fig. 284. — Élément Daniell.

155 years

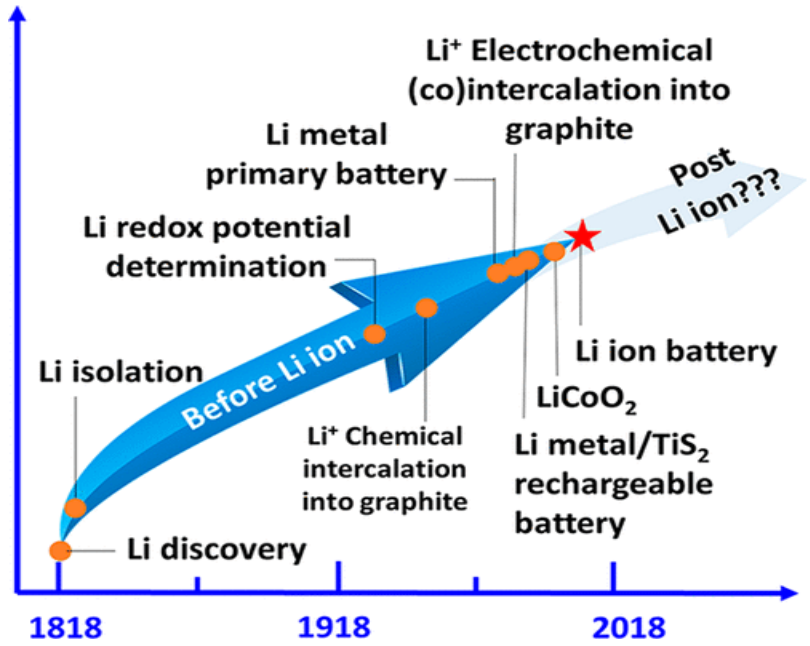




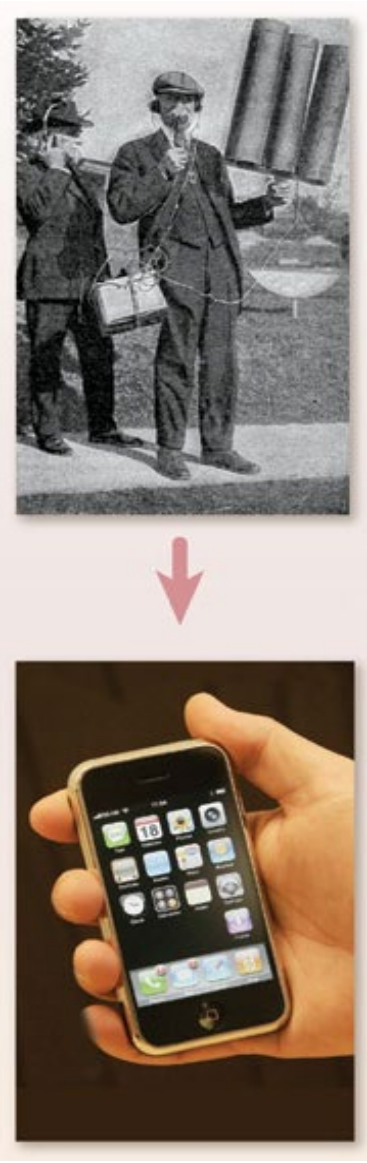
Daniell cell (1836)

Commercial Li-ion Rechargeable Battery (1991)

Wonders of Lithium-ion Batteries



Chem. Rev. 2018, 118, 23, 11433−11456



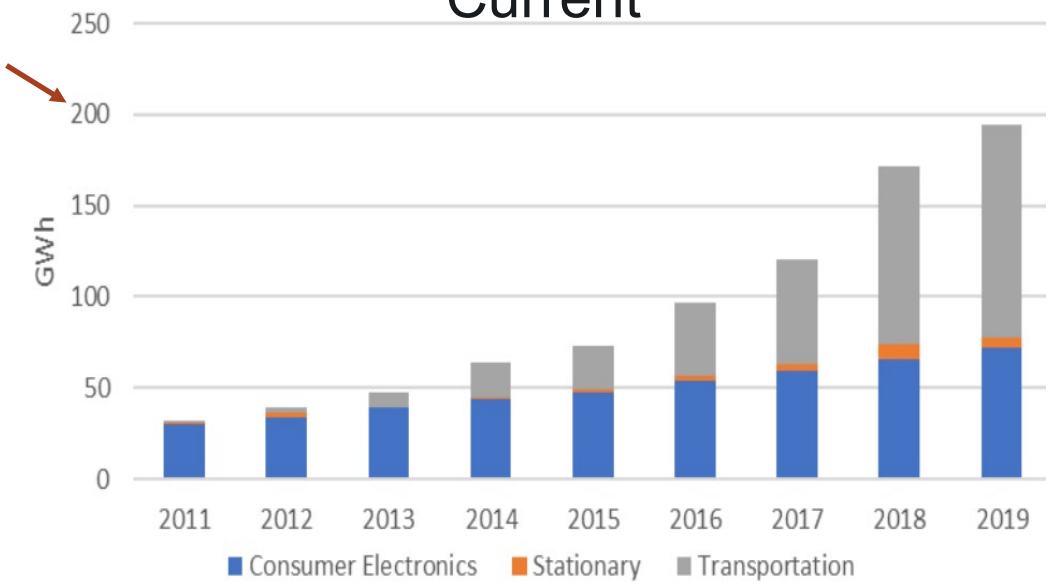
What's next revolution?

M. Armand , J.-M. Tarascon, *Nature* **451**, 652-657

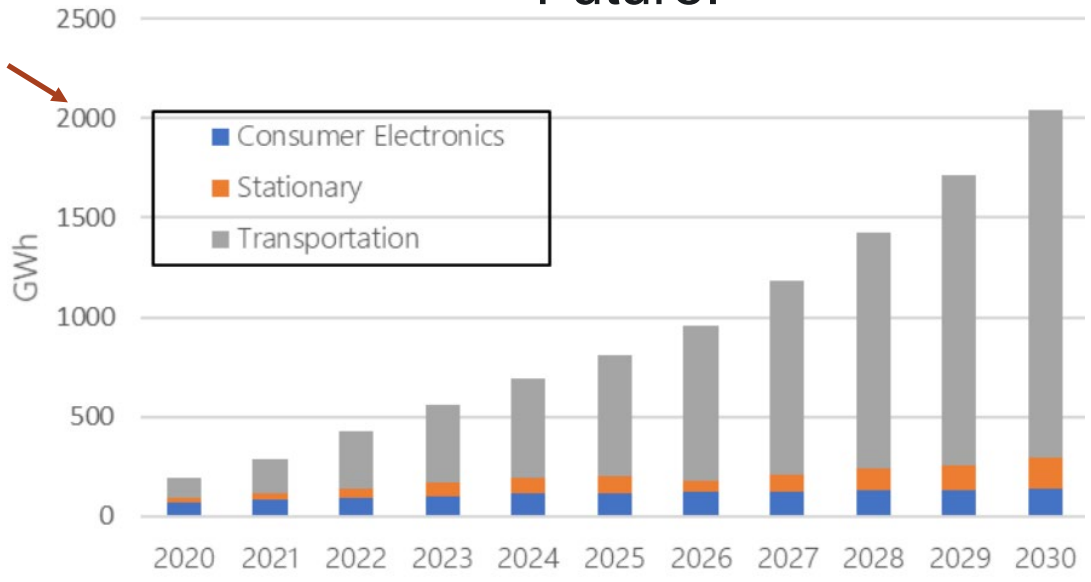
Rapid Demand Growth of Electric Energy Storage (EES)

New electric energy storage (EES) materials and systems need to be developed and validated to meet the growing demand.

Current



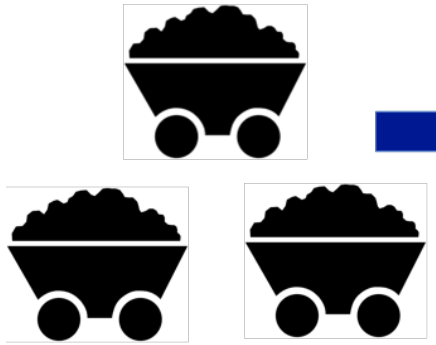
Future!



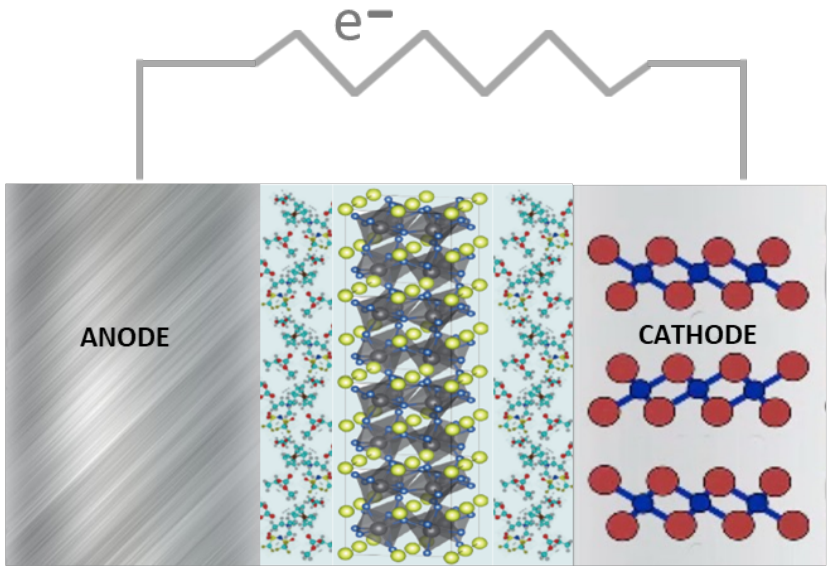
Bloomberg New Energy Finance, "Electric Vehicle Outlook 2020," BloombergNEF, New York, 2020.

Rapidly growing demand for energy storage brings significant challenge!

Science can deliver safer, cheaper and efficient EES



Raw Materials Supply Chain

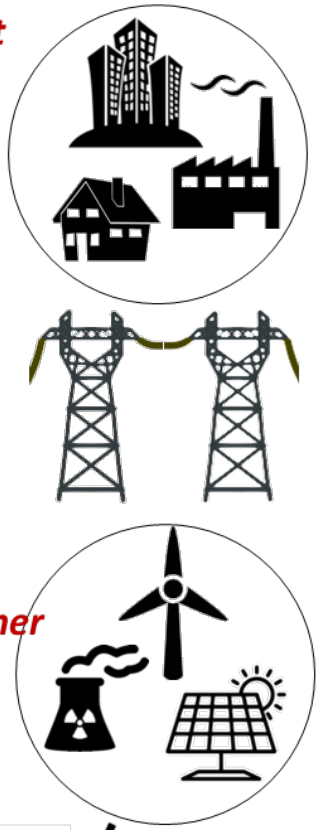


Batteries

Regional passenger flight requires >800 Wh/kg

Many Emerging Applications

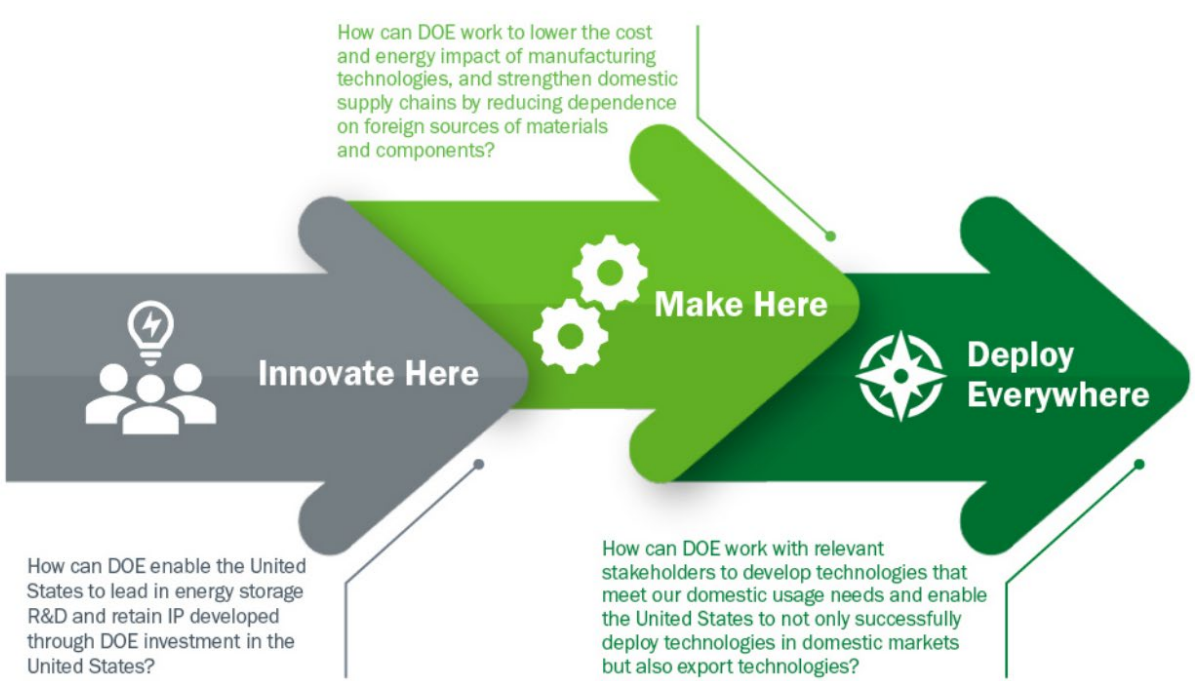
Stabilize against 10 consecutive days of cloudy or calm weather

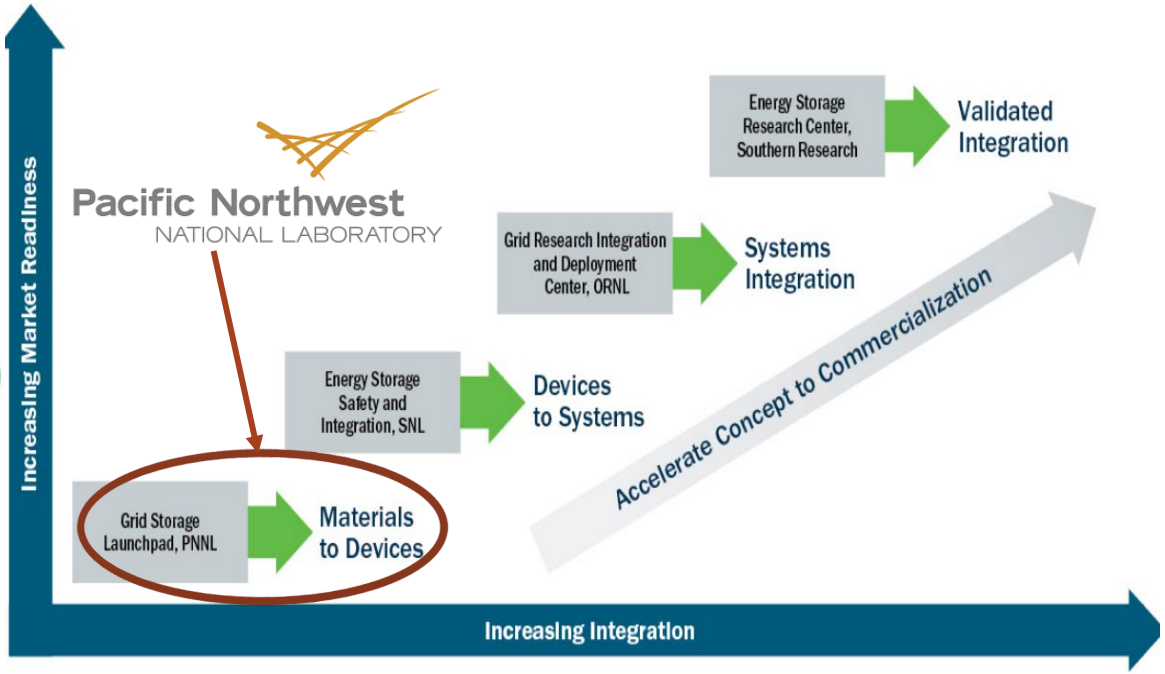


Market pull selects winning battery technologies
Materials supply chain constrains cost and scale up

The Ecosystem Develops as a Whole
A Diversity of Batteries for a Diversity of Uses

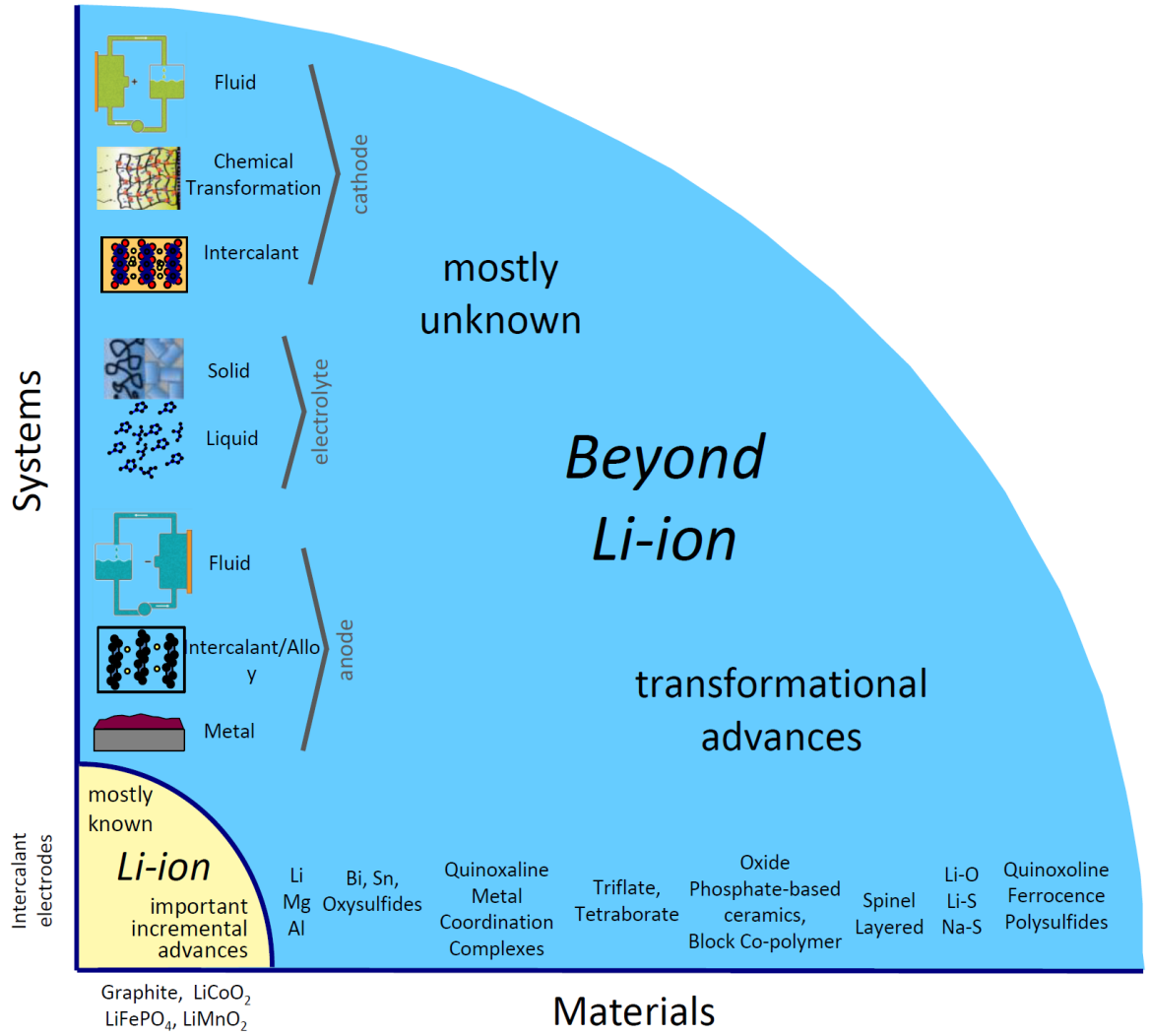
US Department of Energy (DOE) - Energy Storage Grand Challenge Road Map

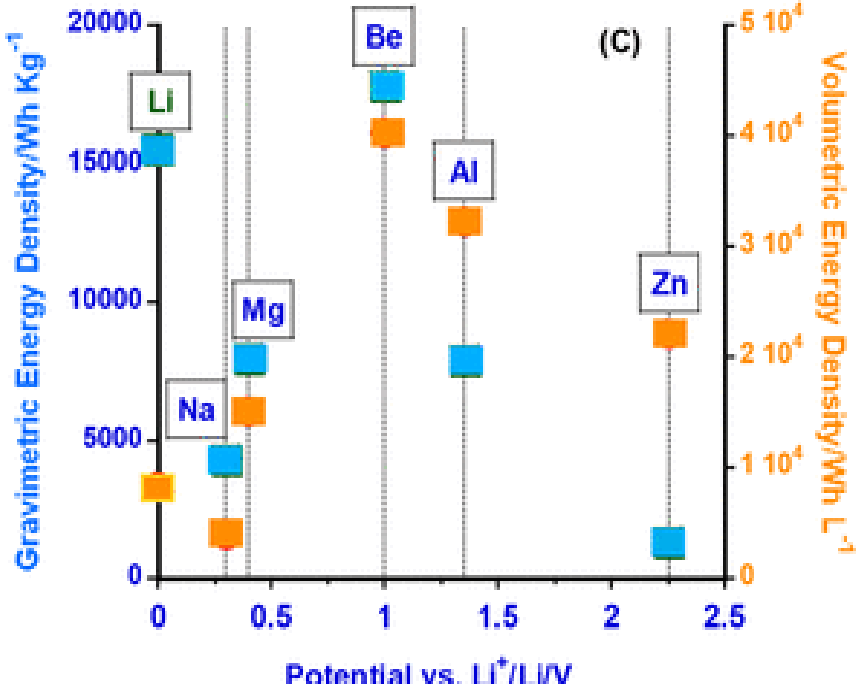




PNNL has unique expertise and capabilities to innovate materials for energy storage devices.

Beyond Li-Batteries Space is Vast, Rich and Unknown





Chem. Rev. 2018, 118, 23, 11433−11456

Joint Center for Energy Storage Research

Transform electrochemistry and energy storage science with disruptive new materials deliberately constructed from the bottom up, where each atom or molecule has a prescribed role in producing targeted material behavior.

JCESR's National Presence

18 partners
6 national labs
11 universities
1 private company

Northwest, Pacific Northwest events: Wind energy

Bay Area event: EVs, Solar energy

First international Li-S event in the U.S.

Texas event: Wind energy

Southwest event: Grid installations

Southern and Northeast events: Grid resilience

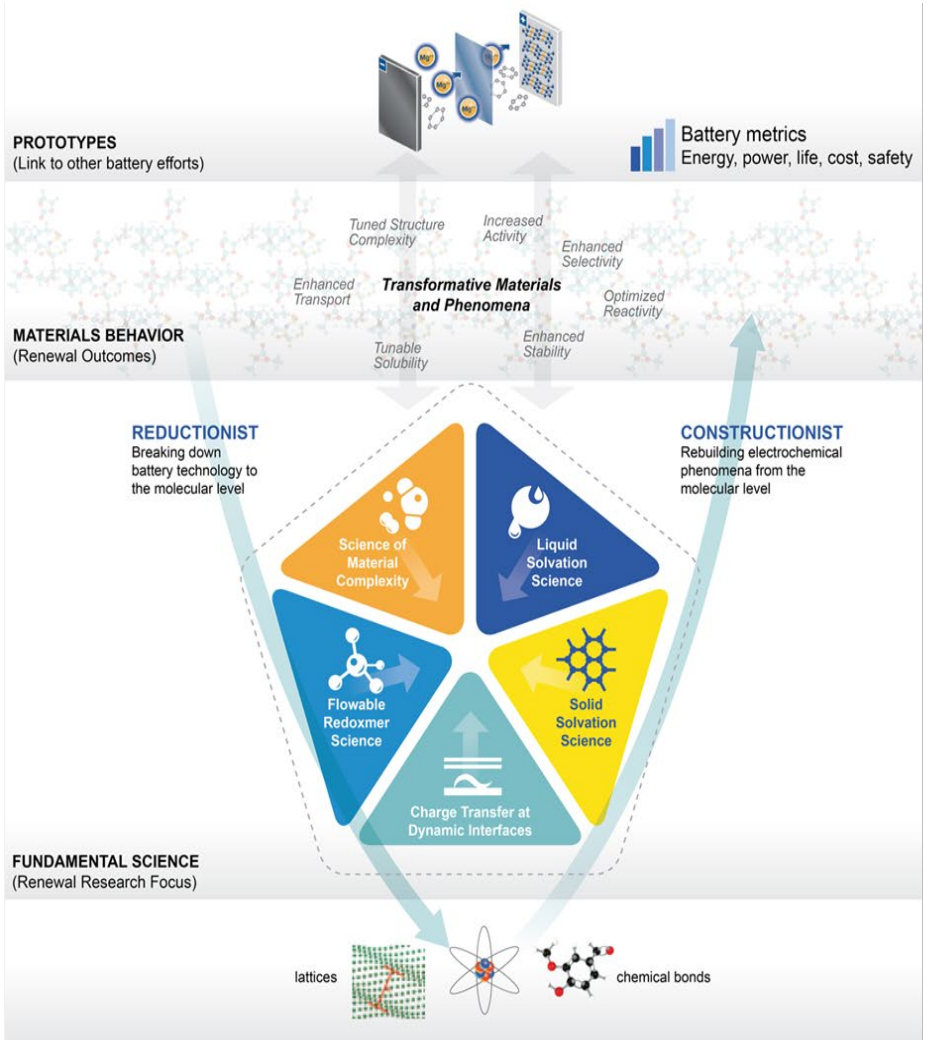
BrightVolt
Pacific Northwest NATIONAL LABORATORY
ViZn Energy
Idaho National Laboratory
Lawrence Livermore National Laboratory
NASA Jet Propulsion Laboratory
SLAC
BERKELEY LAB
Ceramatec
THE UNIVERSITY OF UTAH
National Renewable Energy Laboratory
Sandia National Laboratories
NORTHWESTERN UNIVERSITY
THE UNIVERSITY OF ILLINOIS AT CHICAGO
THE UNIVERSITY OF CHICAGO
Argonne NATIONAL LABORATORY
ComEd
Exelon Corporation
Illinois Institute of Technology
NAATBatt
Navigant
Responsible Battery Coalition
Johnson Controls
Dow Corning
General Motors
UNIVERSITY OF WATERLOO
Cornell University
MICHIGAN
UNIVERSITY OF NOTRE DAME
ILLINOIS
Cummins Inc.
Energizer
Tennessee Valley Authority
Mississippi State University
University of Texas at Arlington
Georgia Institute of Technology
NextEra Energy Resources
Albemarle
Paraclete Energy
Corning Incorporated
GE Global Research
Massachusetts Institute of Technology
24M Technologies, Inc.
United Technologies
Praxair, Inc.
Carnegie Mellon University
Concurrent Technologies Corporation
University of Delaware
DuPont Central R&D
Lockheed Martin Advanced Energy Storage, LLC
ARL
Duracell
NASA Glenn Research Center

JCESR Partner States
100+ JCESR Affiliates in 2(states, 4 countries
13 JCESR Regional Events

JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

www.jcesr.org

Energy storage emerging: A perspective from the Joint Center for Energy Storage Research

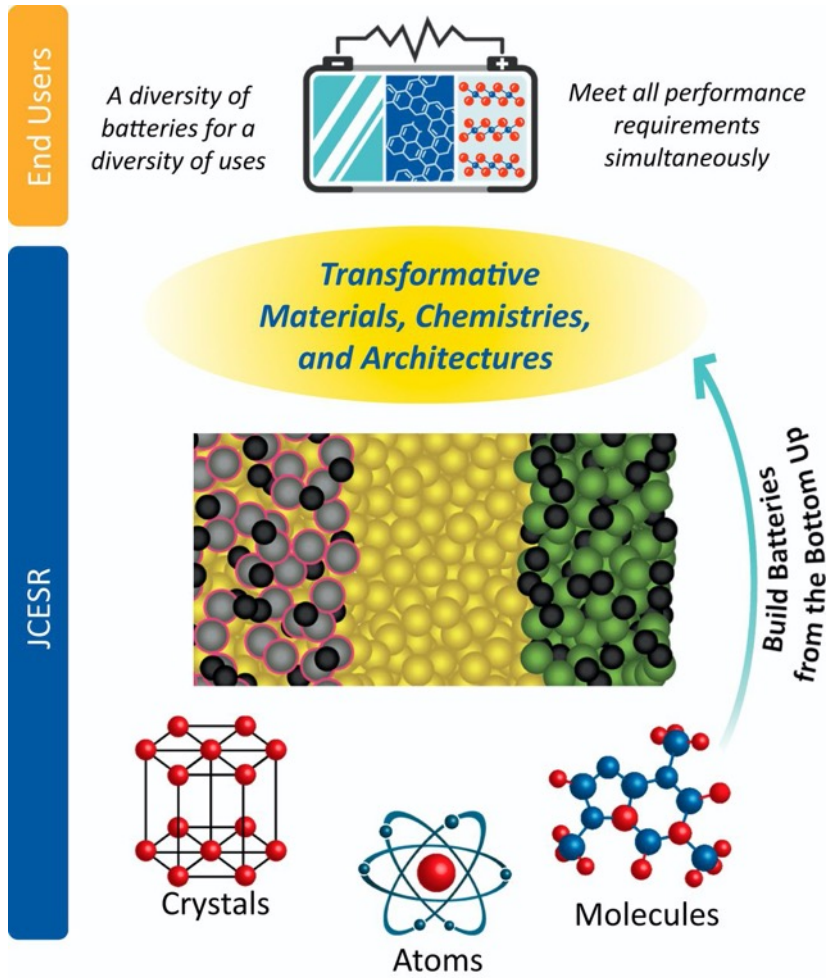


JCESR 2.0 VISION

New materials and phenomena deliberately created from the bottom up using design principles formulated at the atomic and molecular level.

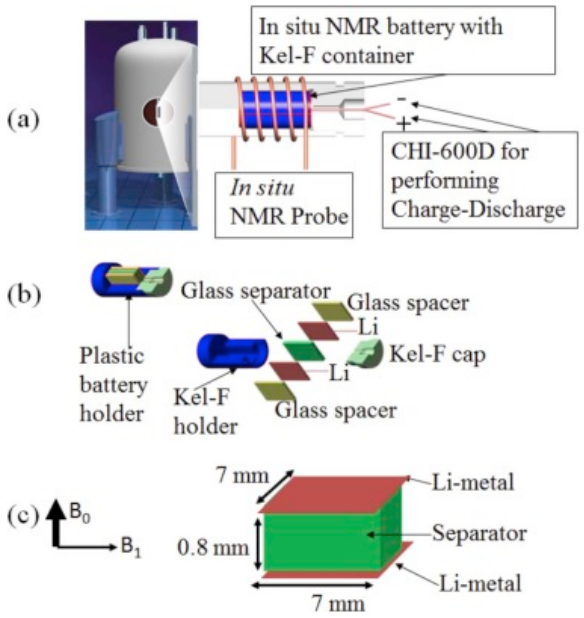
JCESR 2.0 MISSION

- A description of solvation "cages" across the solid-liquid continuum.
- An exhaustive knowledge of redox active multimers with custom design of their complex structure.
- A predictive understanding of the role of defects in solids and heterogeneities at interfaces.

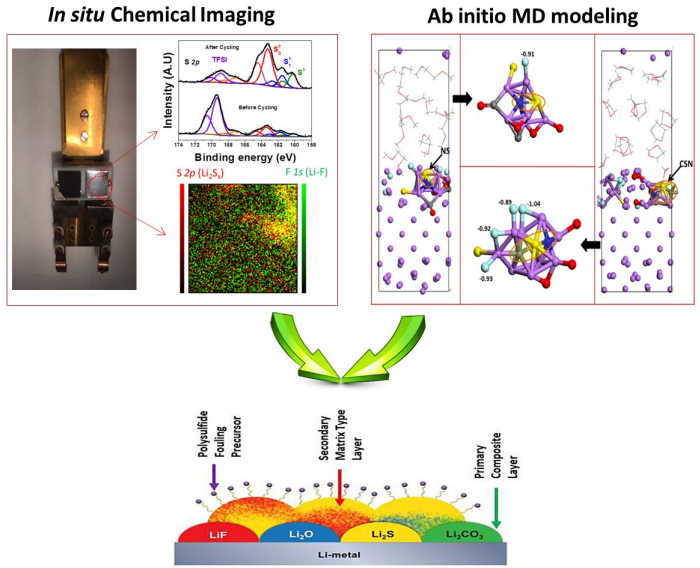


PNNL Build Novel Tools to Study Inner Workings of Battery during charge/discharge cycle

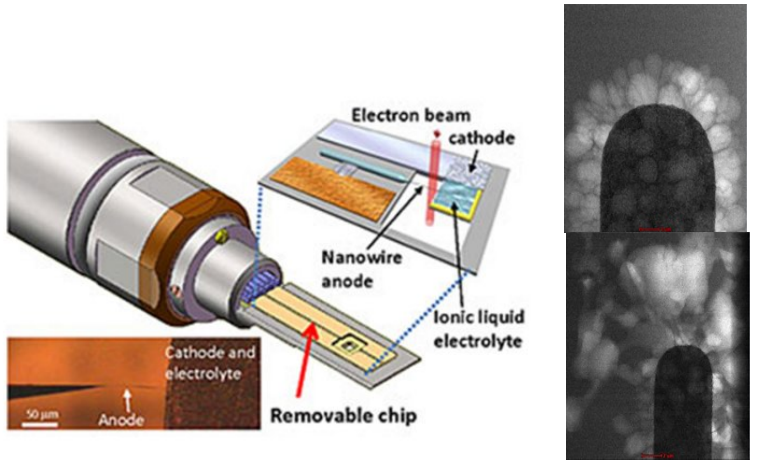
NMR



XPS



TEM

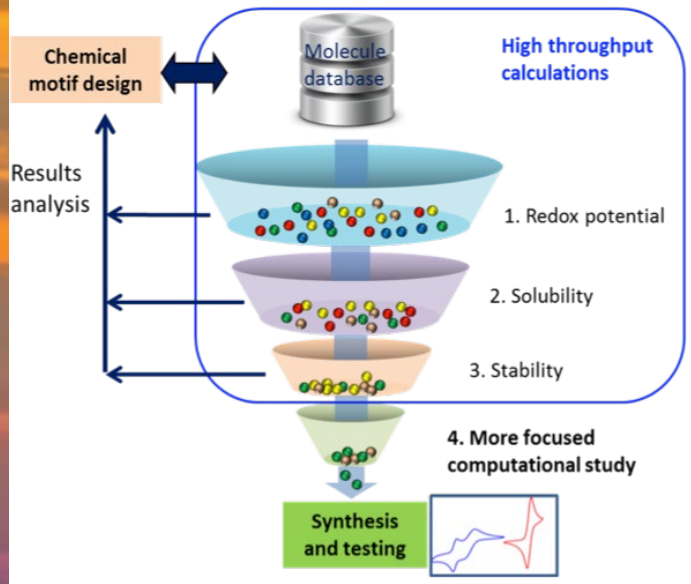


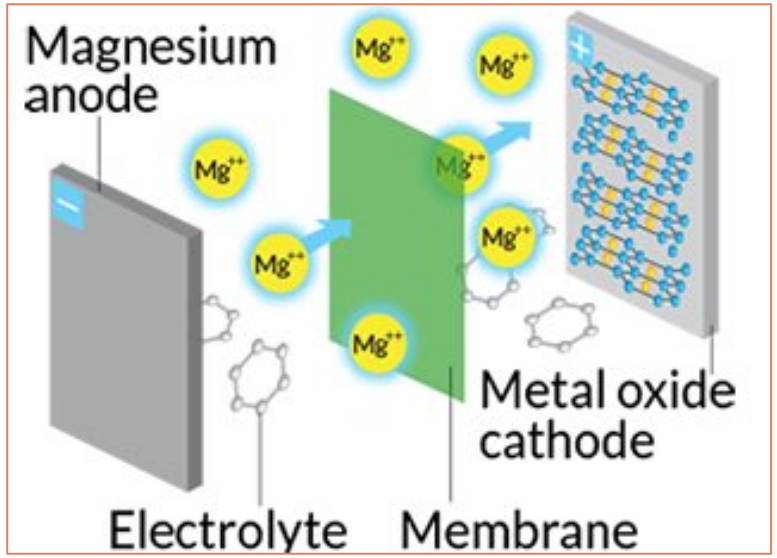
PNNL hosts suite of unique tools to study the materials degradation during charge/discharge process of Li-batteries.

Extremely high-resolution imaging of chemical reactions in lithium-metal batteries to understand how to design long battery lifetimes by watching how batteries degrade in real time.

Recent Success and Remaining Challenges in Designing New Multi-Valent Battery Materials

Electrolyte Genome



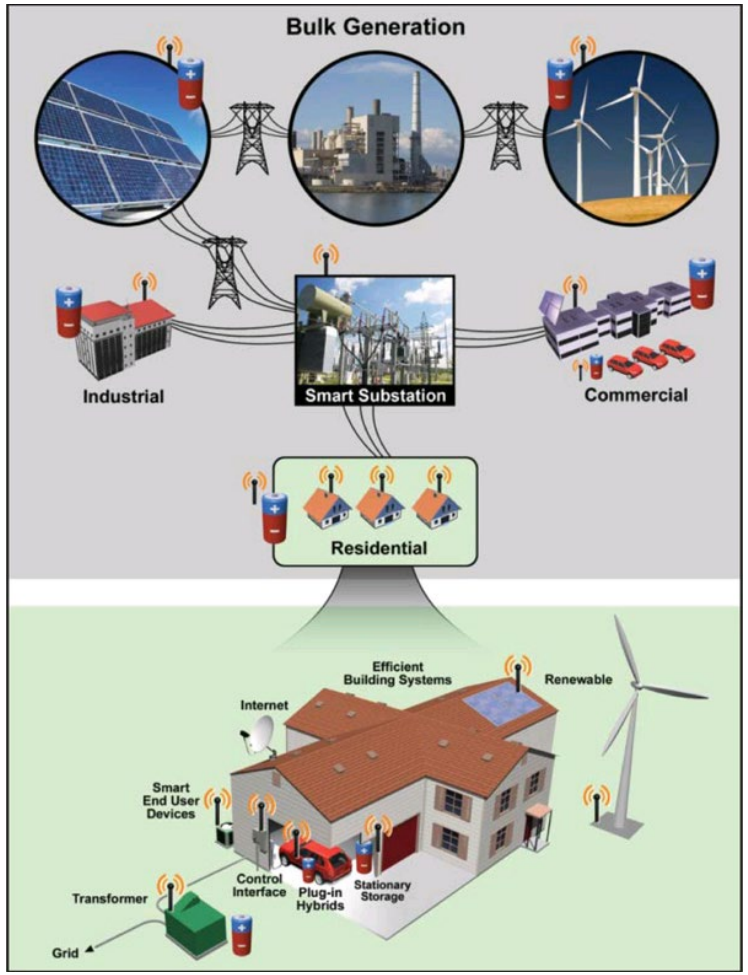


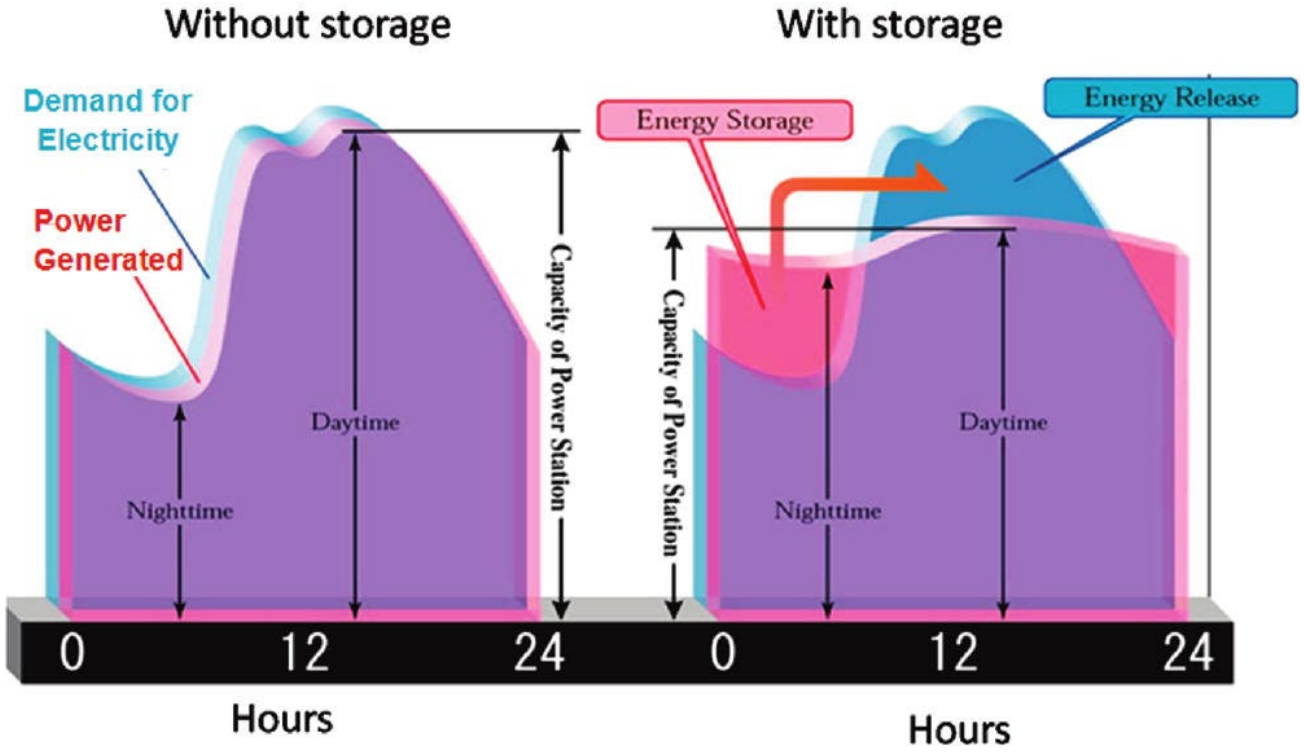
Materials Project

- •14,615 New structures
- •15,789 VASP runs
- •2+ Million CPU hours
- •10,119 calculations

Recent success in designing electrode and electrolyte materials for rechargeable multivalent batteries are encouraging, but still a long way to go !

Need for Large Scale EES – Reliable & Resilient Electrical Grid





DOE OE's Priority:

North American Energy Resiliency Model
Megawatt Scale Grid Storage

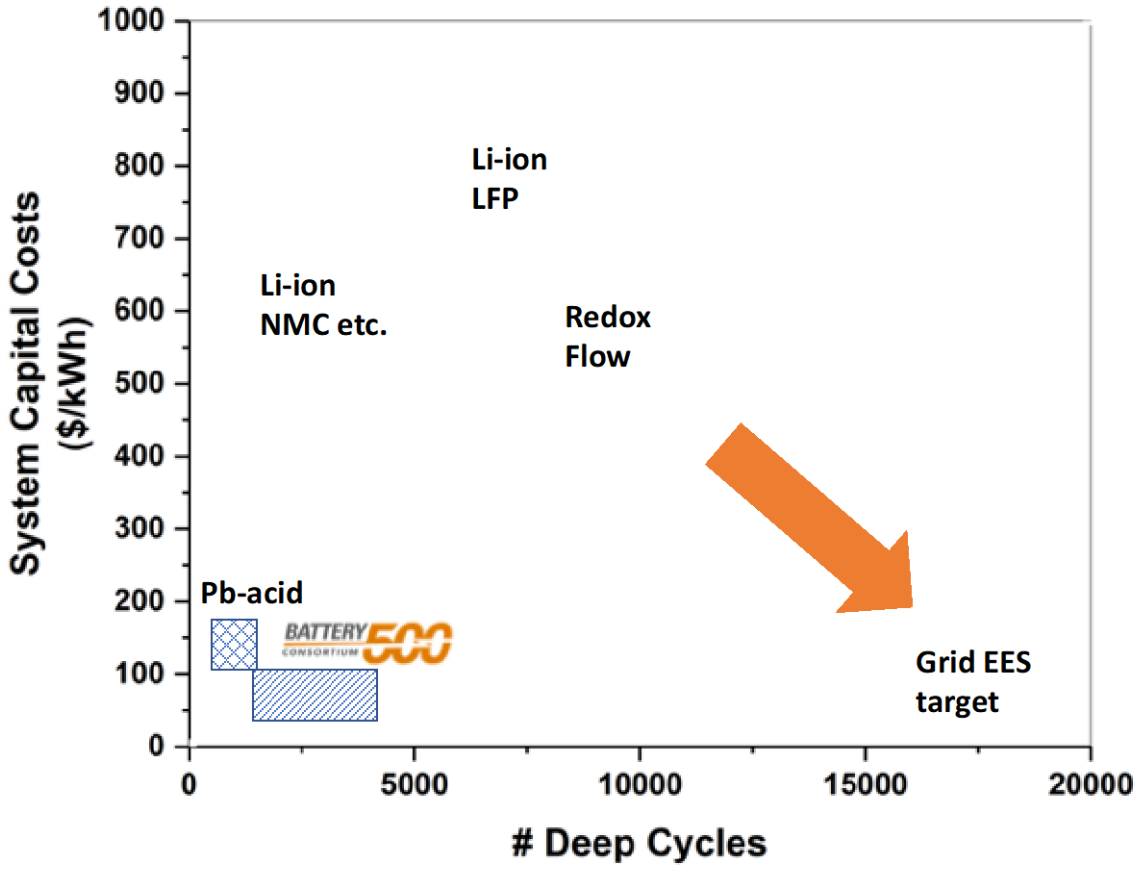
Technology and Market Challenges

Need new approach to accelerate the energy materials innovation.

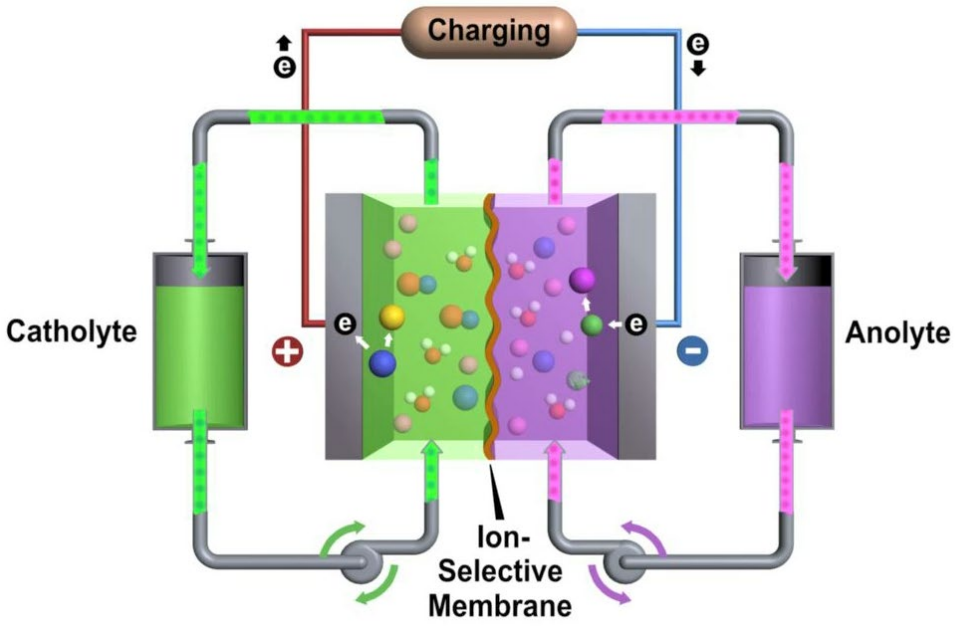
- Safety risks
- Significant cost reduction is needed for greater market penetration.
- Critical materials availability and sustainability.

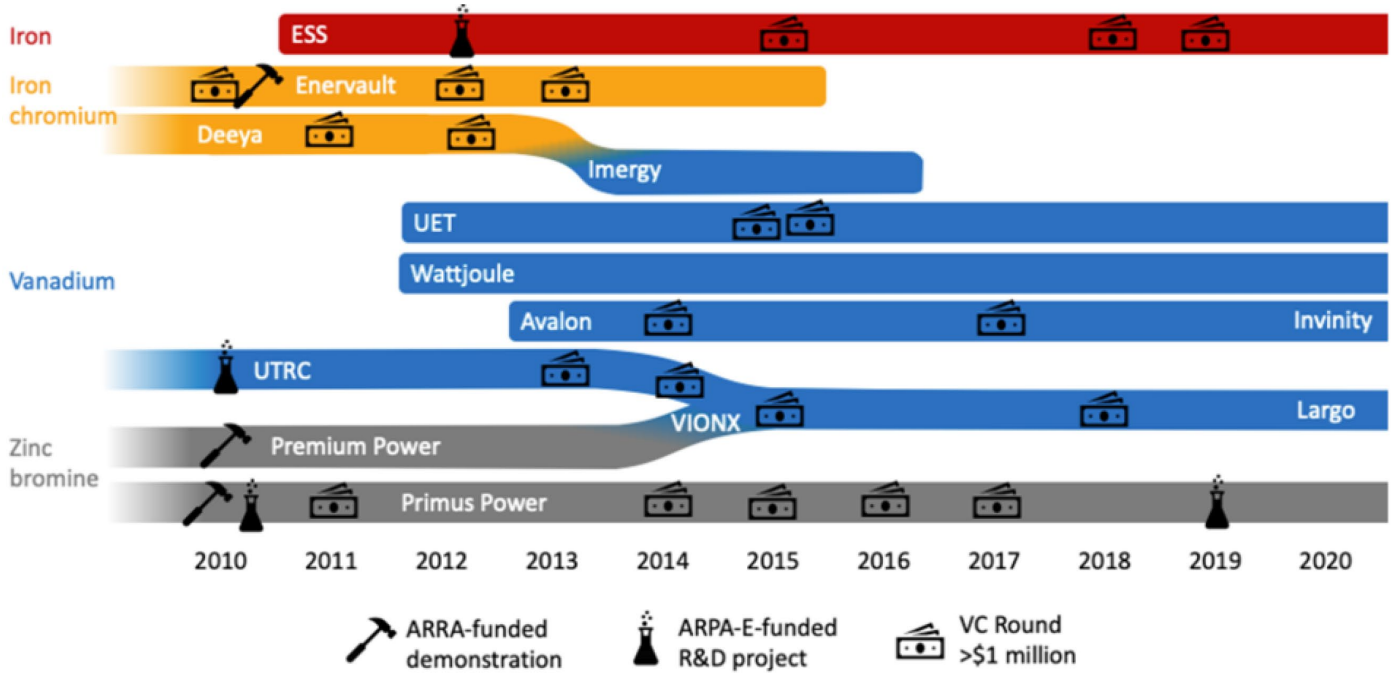
April 2019, McMicken, AZ, 2MW / 1MWh
8 Firefighters hospitalized

The energy density of lithium-ion battery was improved < 2% per year over the last 40 years.



Redox Flow Batteries – Grid Scale EES





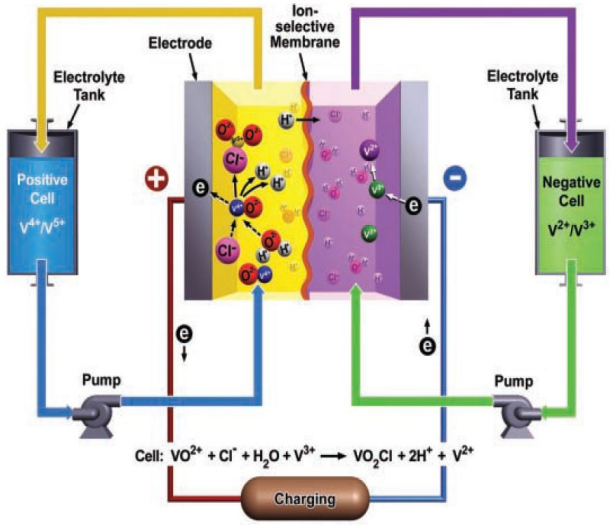
UET: UniEnergy Technologies.
UTRC: United Technologies Research Center.

ITIF | INFORMATION TECHNOLOGY & INNOVATION FOUNDATION

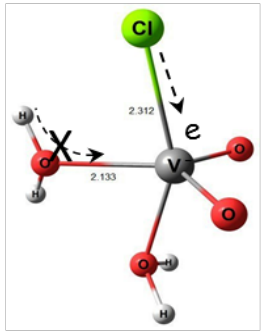
Promising technology for grid energy storage

- High safety
- Potential to reach DOE cost target

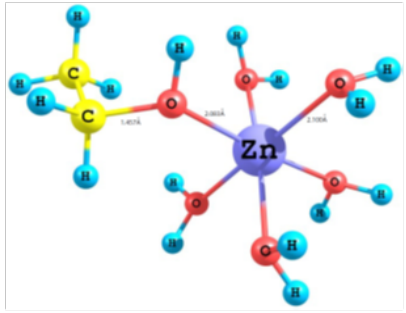
PNNL build novel and viable electrolytes for redox flow batteries (RFB)



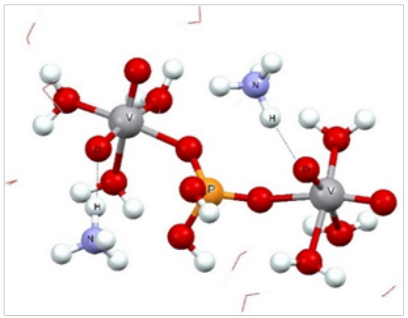
Mixed Acid



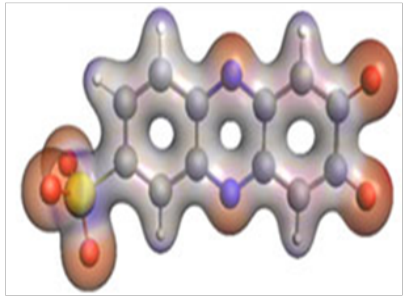
Zn-I electrolyte



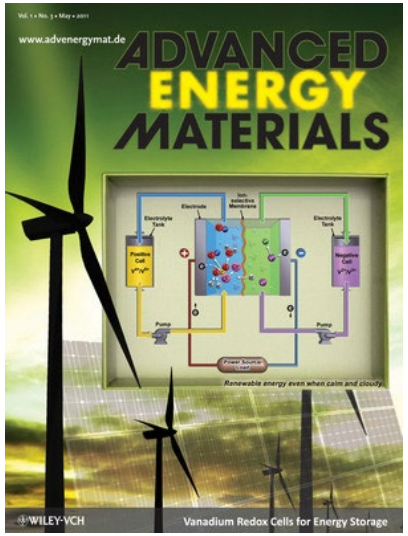
Bi-additives



Organic-Flow



Molecular design and engineering through tuning solvate structure and dynamics



ARTICLE

Received 24 Oct 2014 | Accepted 14 Jan 2015 | Published 24 Feb 2015 DOI: 10.1038/ncomms7303 OPEN

Ambipolar zinc-polyiodide electrolyte for a high-energy density aqueous redox flow battery

Bin Li[1], Zimin Nie[1], M. Vijayakumar[1], Guosheng Li[1], Jun Liu[1], Vincent Sprenkle[1] & Wei Wang[1]

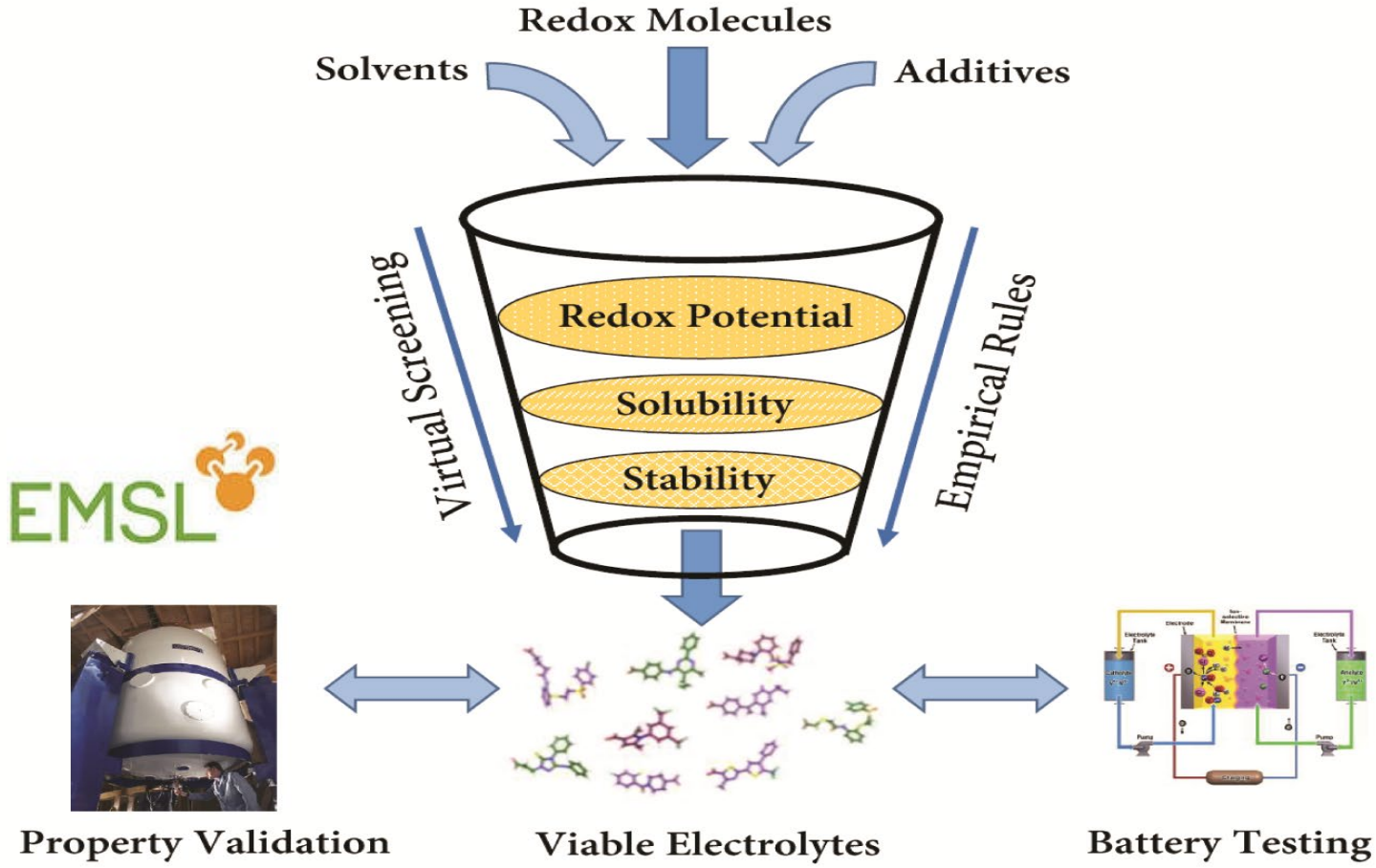
Redox flow batteries are receiving wide attention for electrochemical energy storage due to their unique architecture and advantages, but progress has so far been limited by their low energy density (~25 Wh l^{-1}). Here we report a high-energy density aqueous zinc-polyiodide flow battery. Using the highly soluble iodide/triiodide redox couple, a discharge energy density of 167 Wh l^{-1} is demonstrated with a near-neutral 5.0 M ZnI_2 electrolyte. Nuclear magnetic resonance study and density functional theory-based simulation along with flow test data indicate that the addition of an alcohol (ethanol) induces ligand formation between oxygen on the hydroxyl group and the zinc ions, which expands the stable electrolyte temperature window to from −20 to 50 °C, while ameliorating the zinc dendrite. With the high-energy density and its benign nature free from strong acids and corrosive components, zinc-polyiodide flow battery is a promising candidate for various energy storage applications.

A biomimetic high-capacity phenazine-based anolyte for aqueous organic redox flow batteries

Aaron Hollas[1], Xiaoliang Wei[1,2]*, Vijayakumar Murugesan[1], Zimin Nie[1], Bin Li[1], David Reed[1], Jun Liu[1], Vincent Sprenkle[1] and Wei Wang[1]*

Aqueous soluble organic (ASO) redox-active materials have recently attracted significant attention as alternatives to traditional transition metal ions in redox flow batteries (RFB). However, reported reversible capacities of ASO are often substantially lower than their theoretical values based on the reported maximum solubilities. Here, we describe a phenazine-based ASO compound with an exceptionally high reversible capacity that exceeds 90% of its theoretical value. By strategically modifying the phenazine molecular structure, we demonstrate an increased solubility from near-zero with pristine phenazine to as much as 1.8 M while also shifting its redox potential by more than 400 mV. An RFB based on a phenazine derivative (7,8-dihydroxyphenazine-2-sulfonic acid) at its near-saturation concentration exhibits an operating voltage of 1.4 V with a reversible anolyte capacity of 67 Ah l^{-1} and a capacity retention of 99.98% per cycle over 500 cycles.

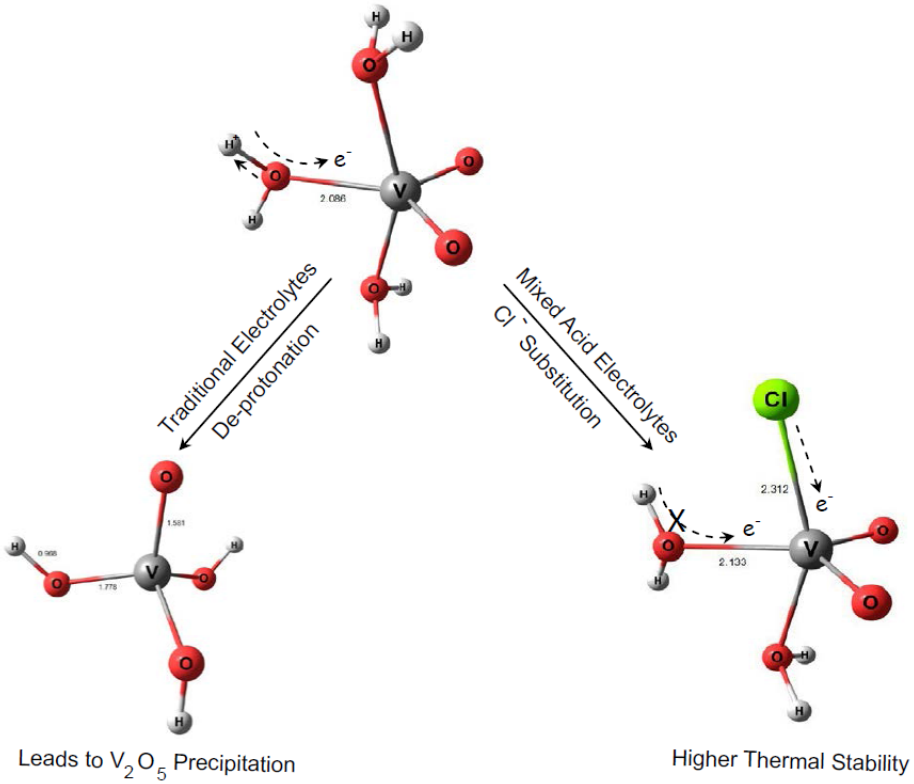
Building Robust Electrolyte Design Module



Virtual screening assisted with empirical rules to down select viable Aqueous electrolytes and subsequent property and battery testing for model validation

Designed a High-Performance Vanadium Electrolyte

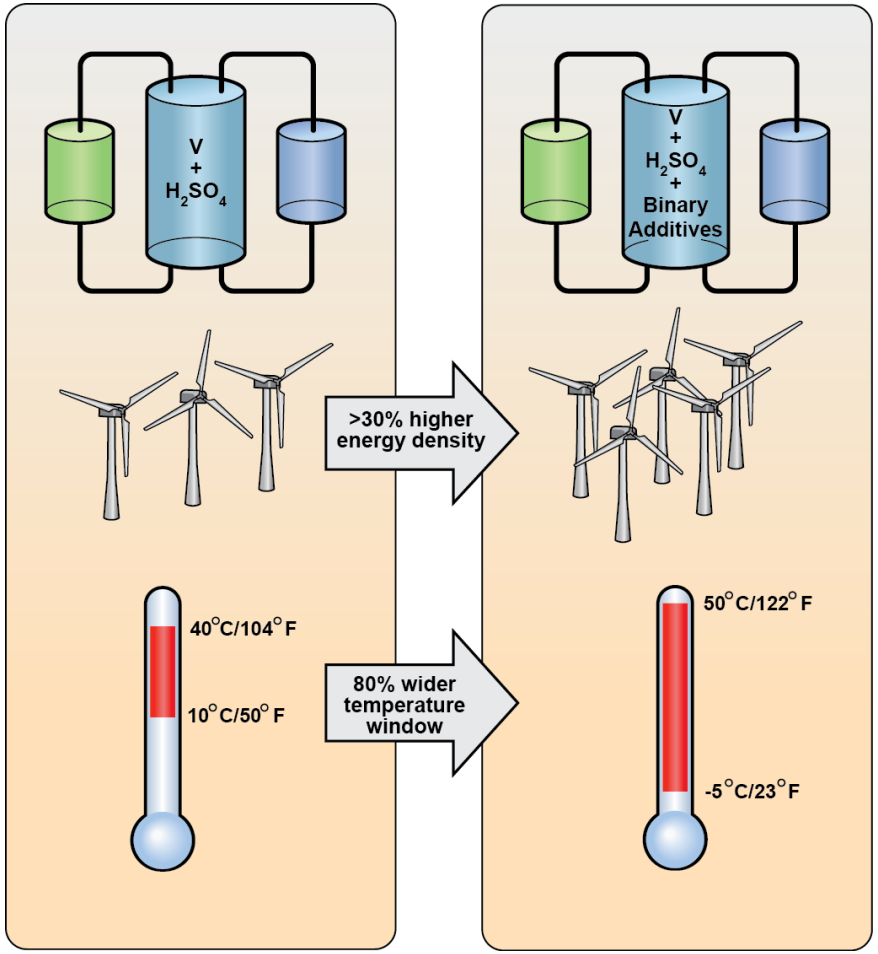
Chloride anion suppress the deprotonation and subsequent precipitation reaction



$$[VO_2(H_2O)_3]^+ + HCl \leftrightarrow VO_2Cl(H_2O)_2 + [H_3O]^+ \Delta H > 0$$

Sulfate and chloride mixed electrolytes showed high energy density and broad operational temperature window

Technology Advancement



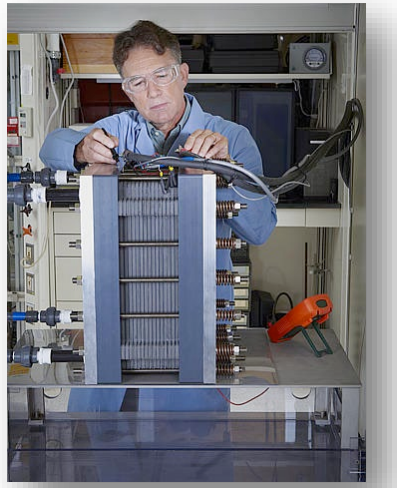
Molecules to Megawatt: Vanadium Battery R&D Story

Traditional Electrolyte

2010

PNNL's Electrolyte

HCl addition prevents deprotonation increasing temperature stability by 80% and energy density by 70%



PNNL kW lab scale demonstration of technology

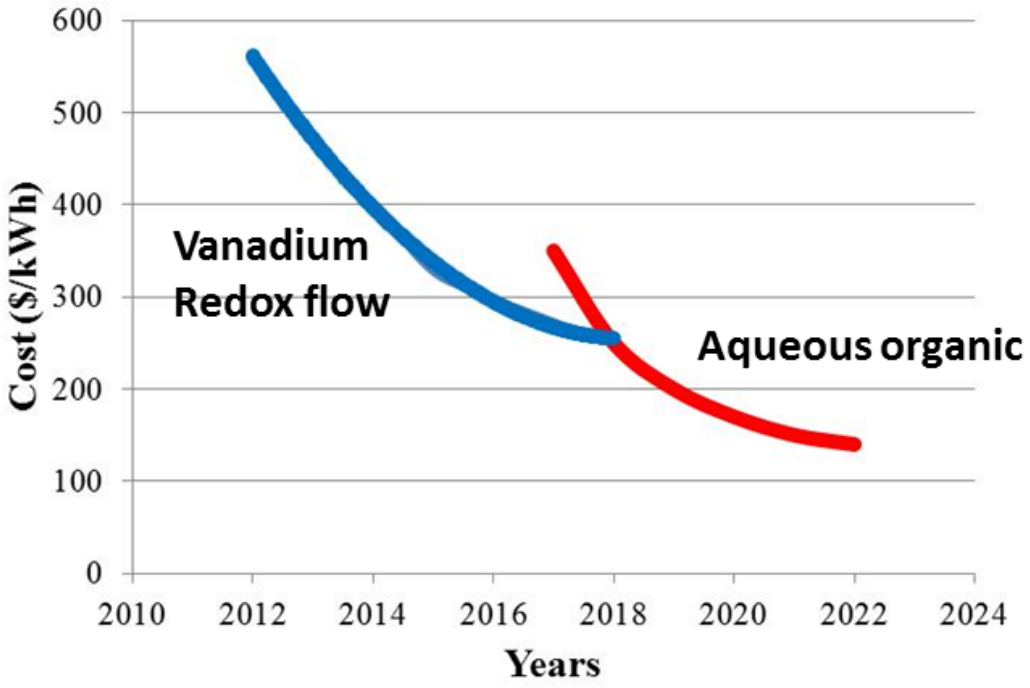
WA Governor Jay Inslee, UniEnergy CEO Gary Yang, OE Asst. Sec. Pat Hoffman at CEF kickoff June 2014

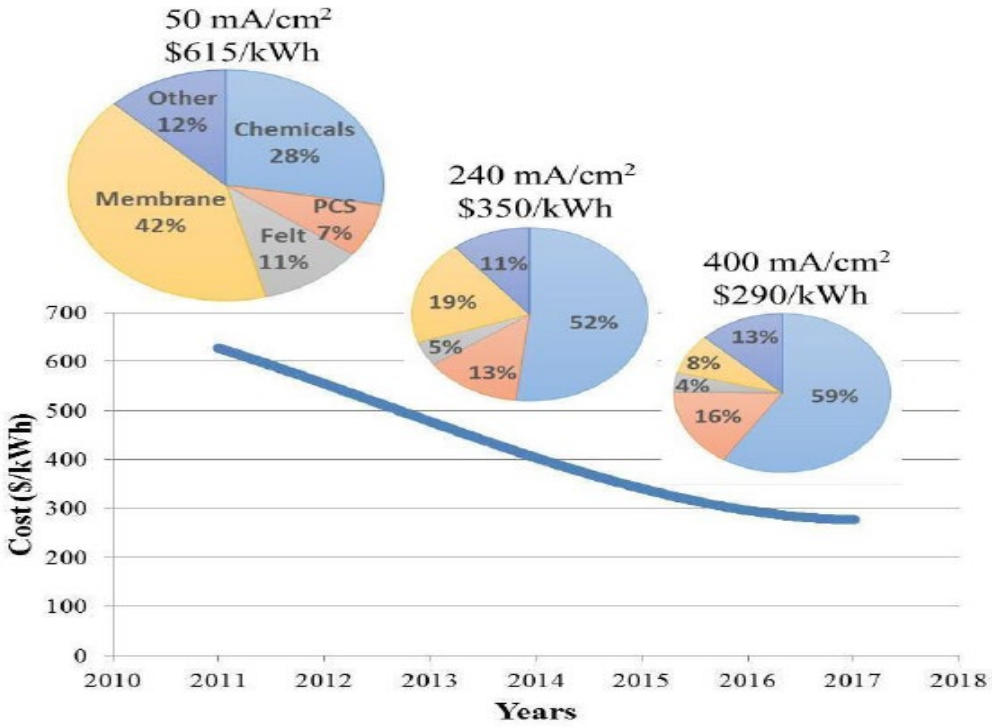
Avista/UniEnergy 1 MW/4 MWh System installation February 2015, commissioned in June.

Aqueous-Soluble Organic RFB is the new frontier

- **Benefits of Organics**
  - Potentially lower cost
  - Vast library of candidates
  - Systems ranging from pH 0-14
  - Improved electrochemical kinetics
  - Candidates with $2e^-$ redox events

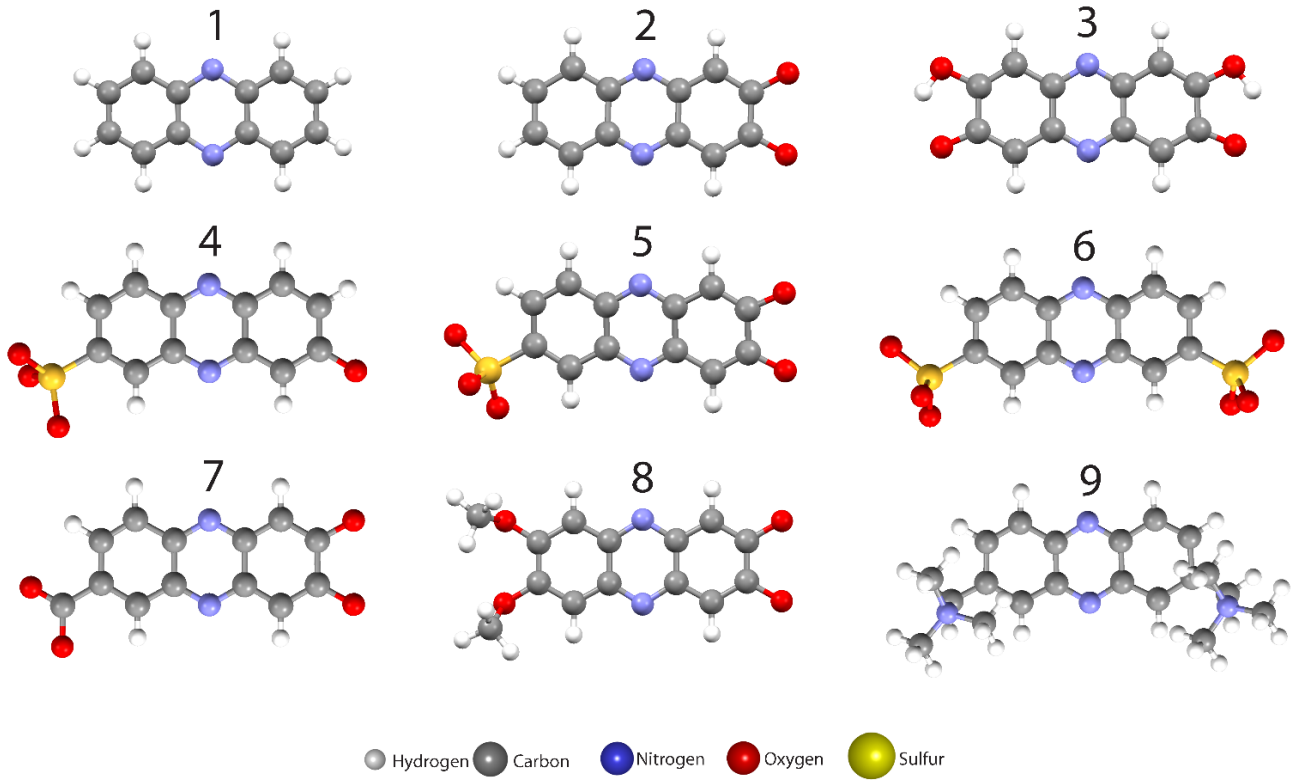
- **Traditional Vanadium RFB**
  - High material cost
  - Capacity loss from crossover
  - Precipitation issues (temperature window)
  - Requires Nafion

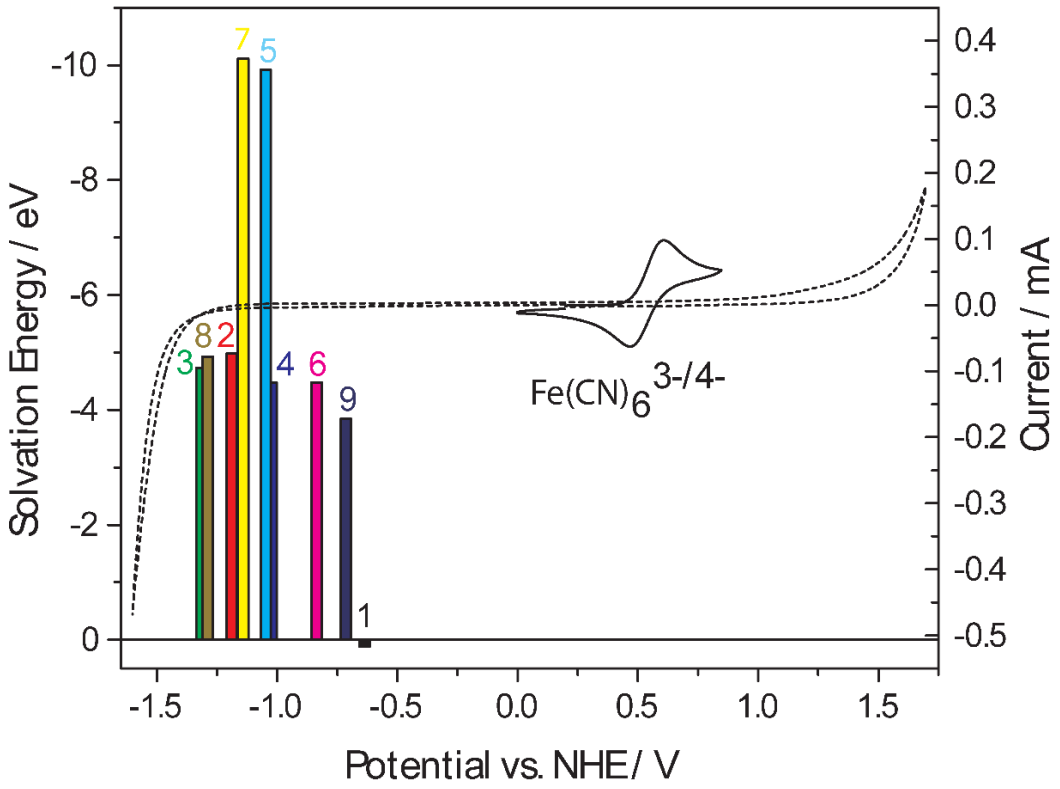




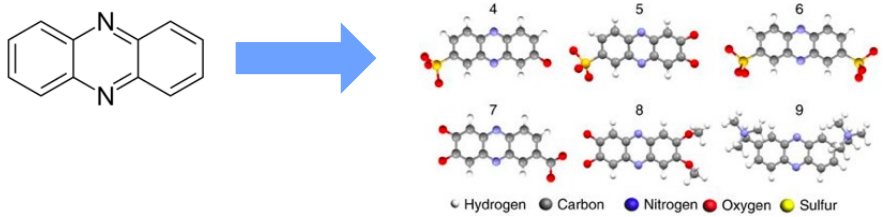
Computationally Guided Molecular Editing

- Target solubilizing groups (pH dependent) and appropriate redox-tuning groups
- Substitute core structure based on readily available reagents and scalable synthetic methods

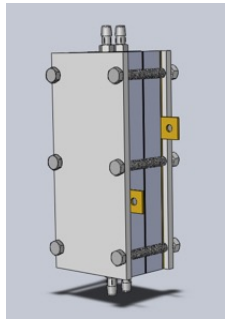


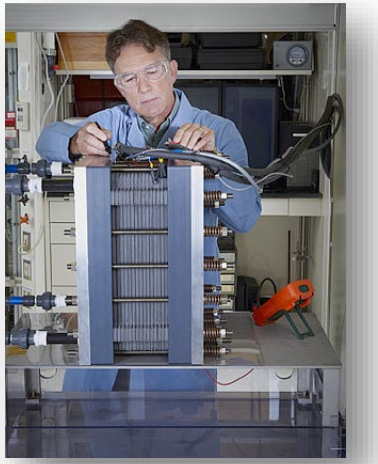


Current fragmented research through trial-and-error approach slows the innovation



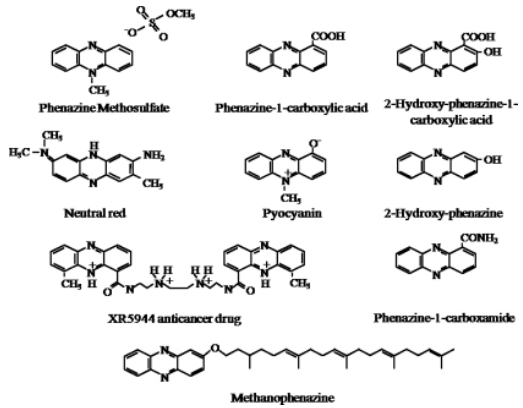
A Hollas, X Wei, V Murugesan, Z Nie, B Li, D Reed, J Liu, V Sprenkle, W Wang
Nature Energy **3**, 508–514, 2018

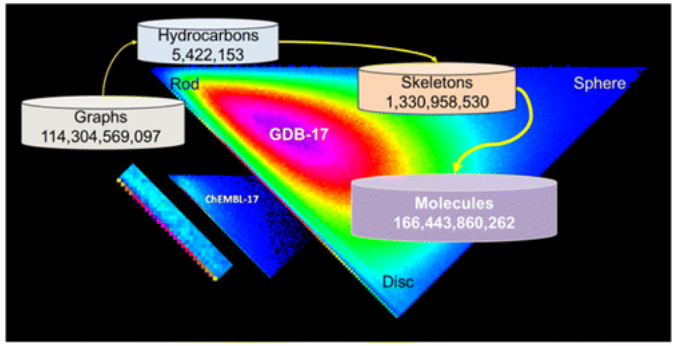




Prototyping in 1kW stack

Known Phenazine derivatives: >6000

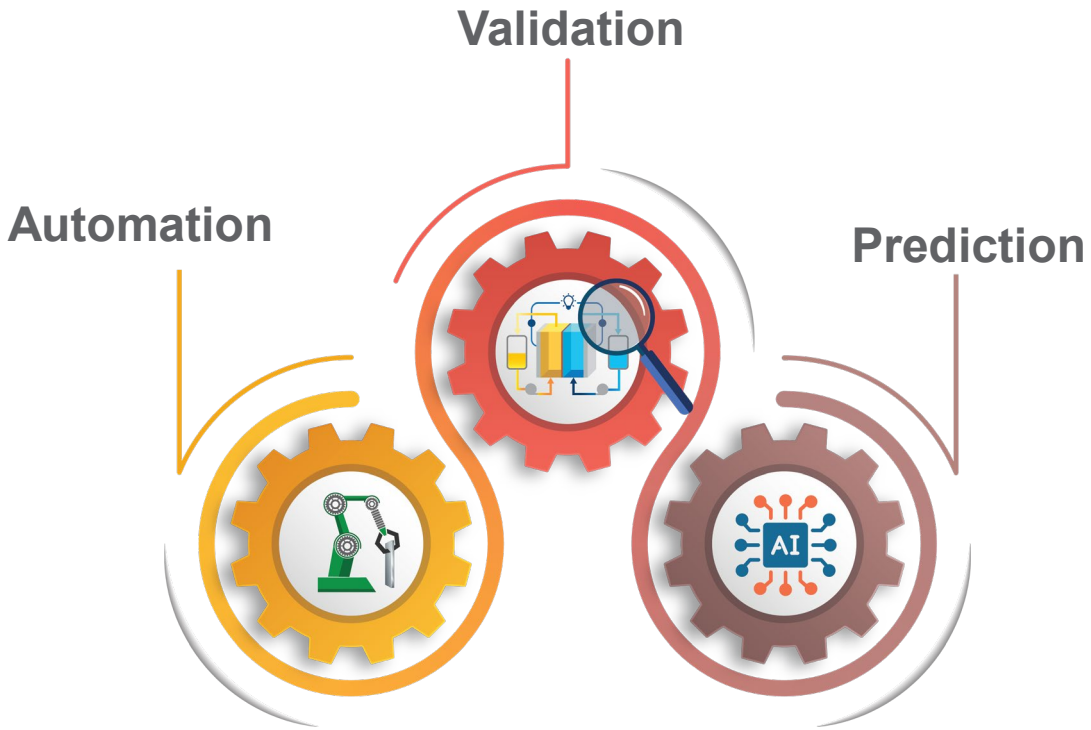




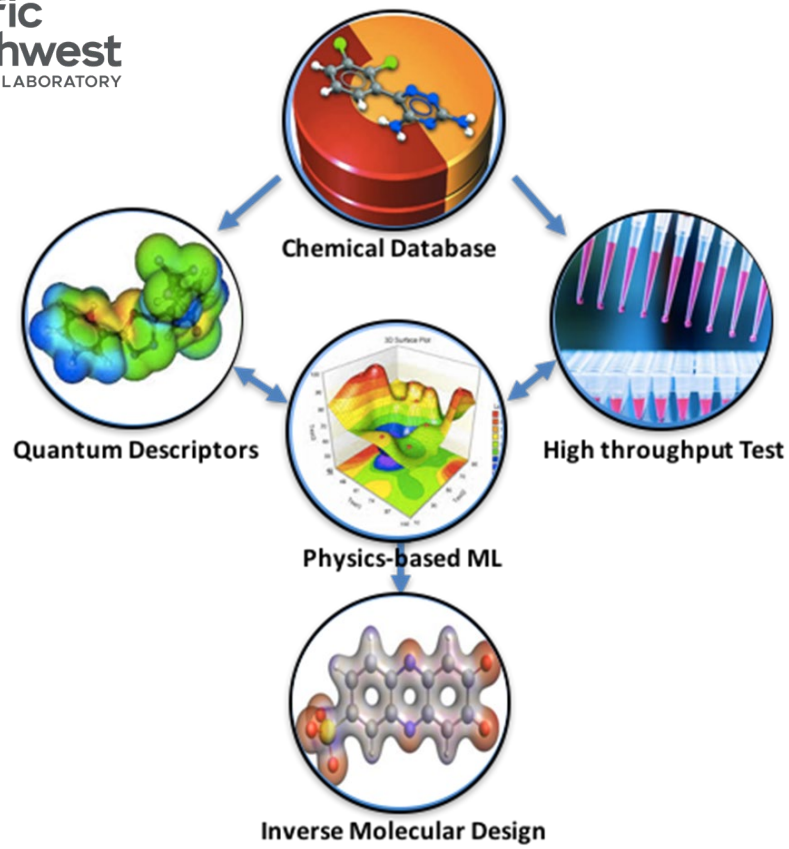
The largest small molecule data-base GDB-17 contains 166.4 billion molecules.

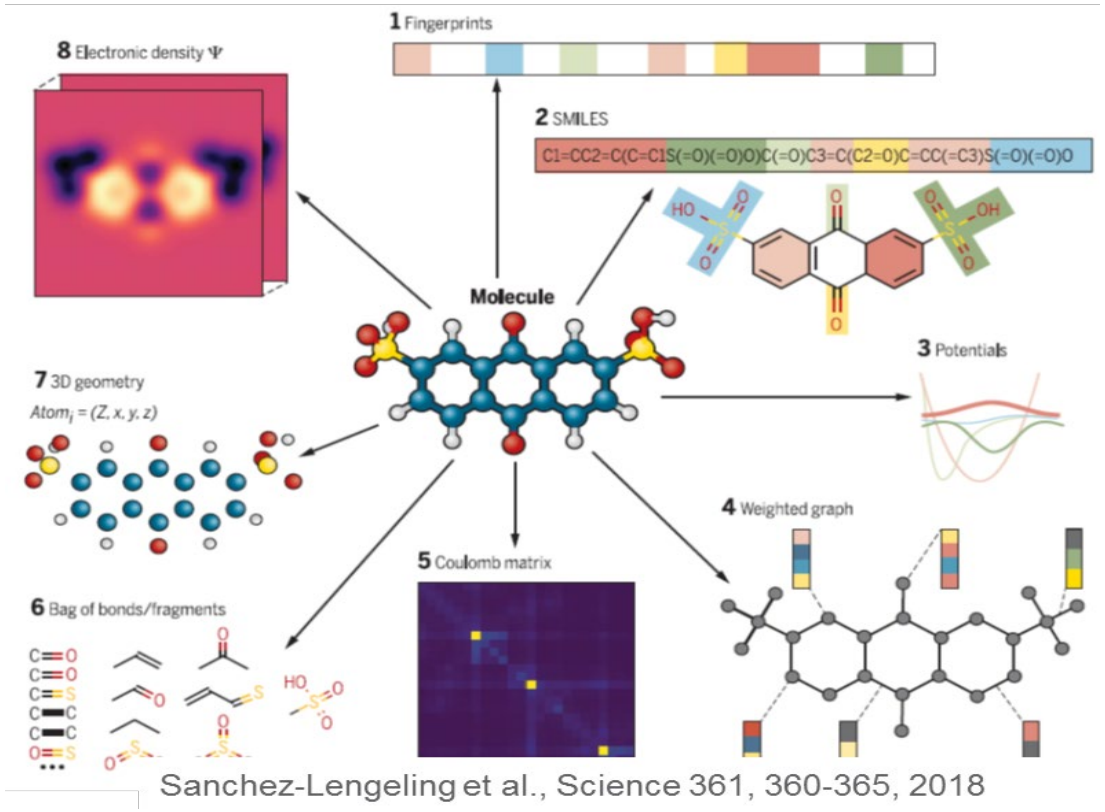
Accelerated Materials Discovery for RFB

“Our goal is to develop a framework for the design of energy storage materials (e.g., redox active molecules) with desired properties (functionality, solubility, electrochemical stability, etc.) through automation (e.g., data sciences and high throughput experimentation)”.



Data Science based Electrolyte Design Formulations





Sanchez-Lengeling et al., Science 361, 360-365, 2018

Vision:
Can recent developments in machine learning (ML) and artificial intelligence (AI), can help us design optimal organic redox flow electrolytes?

Challenges:
No known physics models for predicting solubility and stability.
Enormity organic chemical space (> 10^{11}), demands adequate training data set for reliable ML.

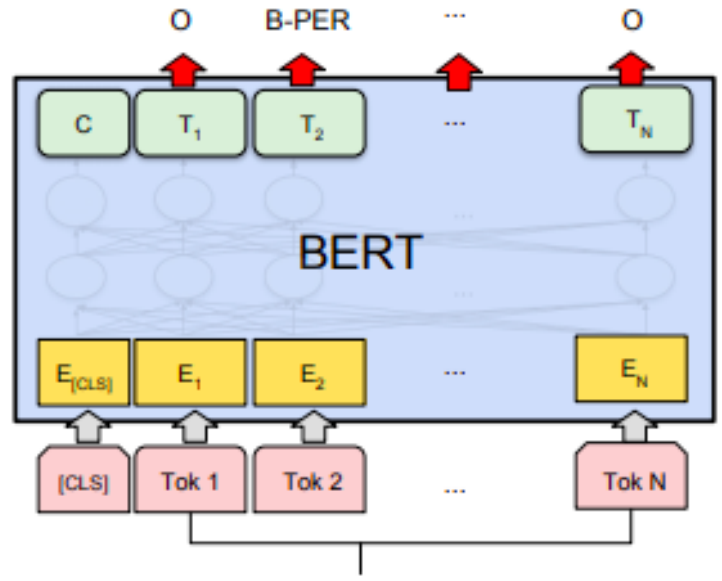
Natural Language Processing for Harvesting Data from Open Source Literatures

https://demo.allennlp.org/named-entity-recognition

When I told John [PER] that I wanted to move to Alaska [LOC], he warned me that I 'd have trouble finding a Starbucks [MISC] there .

For example , benzoquinone [MISC] has a solubility of 0.1 M , while BQDS [MISC] has a solubility of approximately 1.7 M at 25 C.

For example, benzoquinone [chemical] has a solubility of 0.1 M [solubility unit], while BQDS [chemical] has a solubility of approximately 1.7 M [solubility unit] at 25◦C [temperature].



http://jalammar.github.io/illustrated-bert/

- Domain specific NLP tools:
  - SciBERT: pretrained on 1.14M papers from Semantic Scholar (18% CS, 82% biomed)
  - ScispaCy: domain-specific tokenization and sentence splitting

A comprehensive database for organic molecules

The largest database of aqueous solubility and related properties

- Experimental data (> 60,000)
- Quantum descriptor (> 6)
- Molecular descriptor (> 1500)

Experimental data

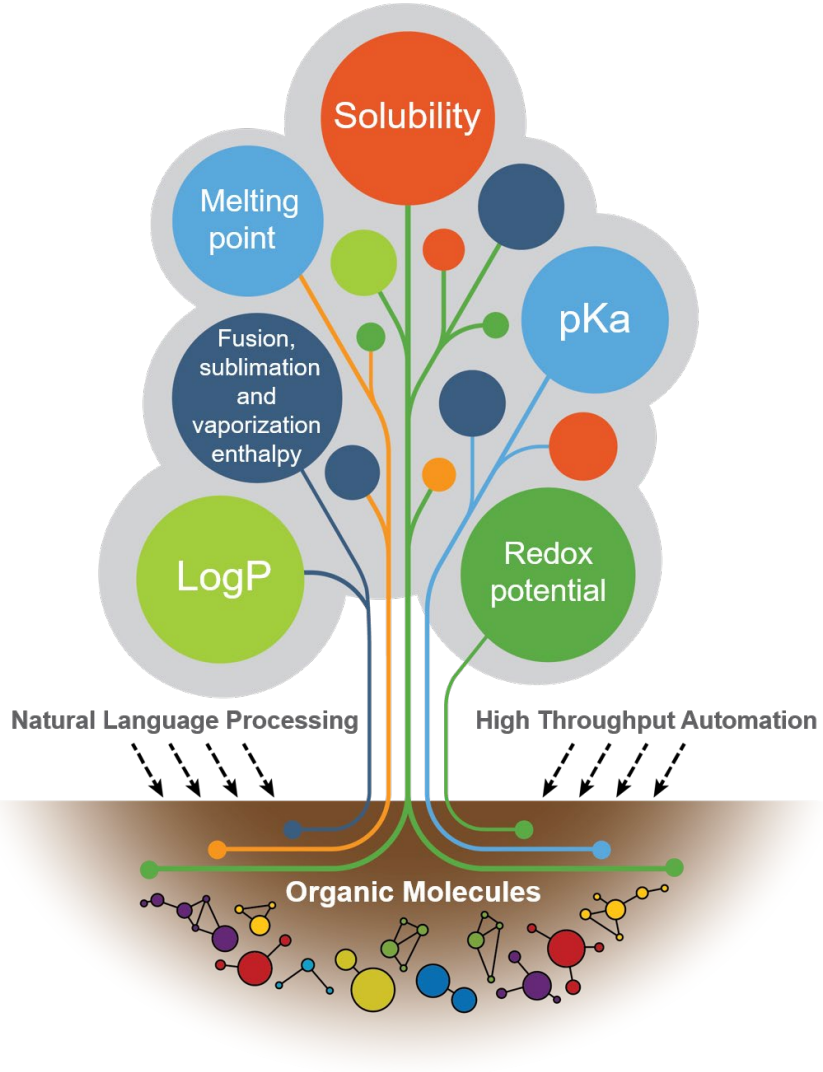
- ~17,000 solubility data
- ~20,000 melting point data
- ~7,000 fusion enthalpy, sublimation enthalpy and vaporization enthalpy data
- ~10,000 pKa data
- ~5,000 redox potential data
- ~4,000 LogP data

Computed data

- Quantum descriptors (solvation energy, dipole moment, quadrupole moment asymmetry, molecular volume, molecular surface area, molecular geometry, etc.)
- Molecular descriptors (Balaban's J index, topological polar surface area, etc.)

Features

- Three independent identifiers (CASRN, SMILES, InChikey)
- Isomeric SMILES
- Multiple subsets



High throughput Experimentation Capabilities

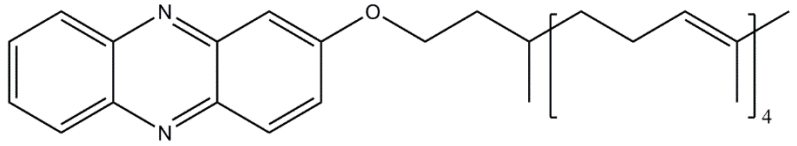
- Installed two robotic systems, *Albert* (N_2 atmosphere) and *Beverley* (Ar atmosphere).
- Handles both liquid (10μl – 10ml) and solid (0.1mg – 25g) samples.
- Vortex mixing (~1000 rpm), heating (<180 °C), centrifugation and filtration
- Working on automating analysis protocols for solubility, density, viscosity and pH testing.
- Staff training and system integrations are in progress.

What can we learn from Nature?

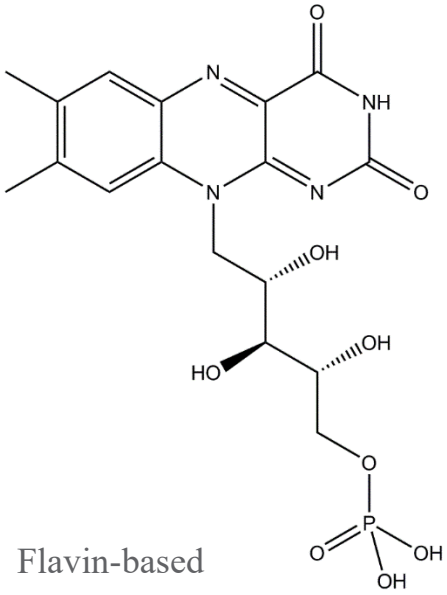
Solubility
$-SO_3^-$, $-CO_2^-$, $-PO_3^{2-}$, $-NH_2$, $-NR_3^+$, -OH
Withdrawing
$-SO_3^-$, $-CO_2^-$, $-PO_3^{2-}$, $-NR_3^+$
Donating
$-NH_2$, -OH

Nature-inspired redox-actives

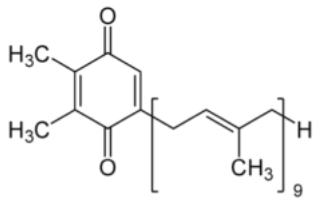
?



Phenazine-based



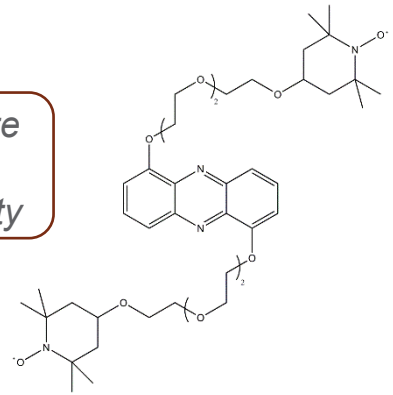
Flavin-based



Quinone-based

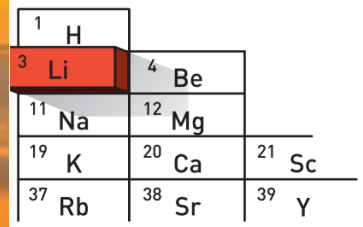
"Inflexible" synthetic route

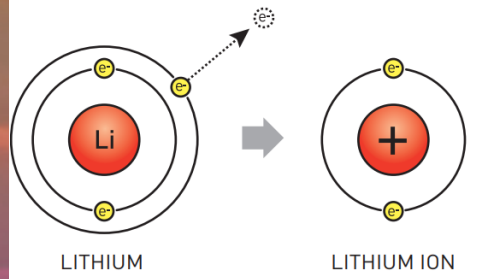
Poor water/DME solubility



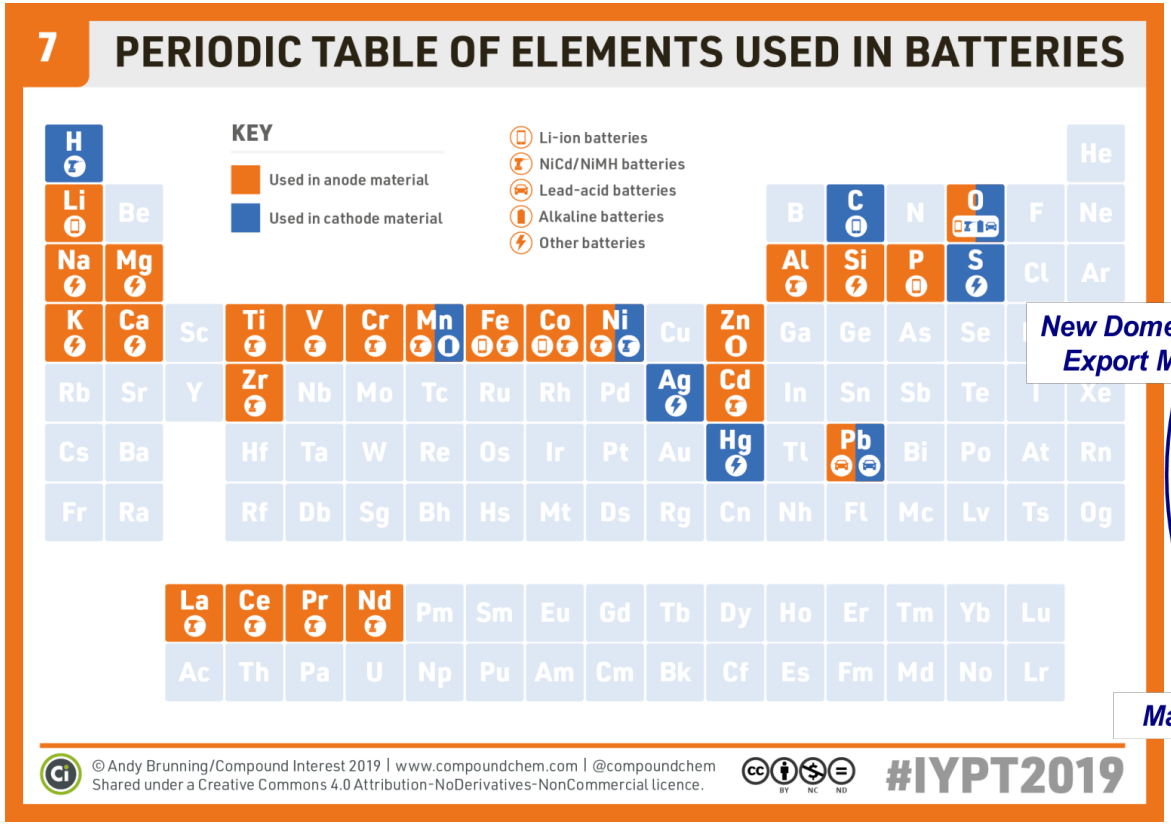
Schubert, *et. al. ACS Energy Lett.* **2016**, *1*, 976.

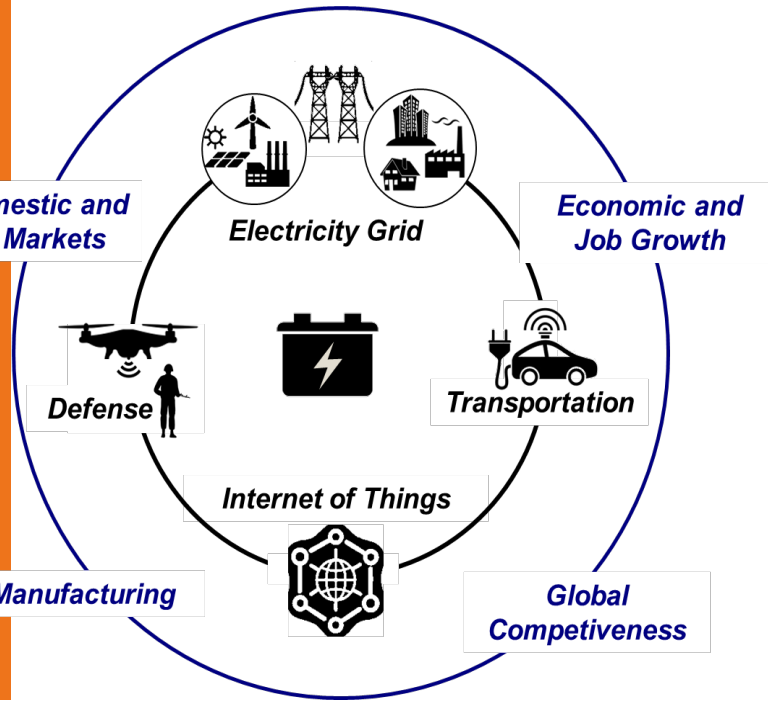
Electrical Energy Storage is Evolving !





©Johan Jarnestad/The Royal Swedish Academy of Sciences





PNNL team is focused on designing transformative and Innovative materials for future energy storage systems.

Vijay Murugesan
Physicist

(509) 371-6540 Work
vijay@pnnl.gov

3335 Innovation Blvd K8-93
Richland, WA 99354
www.pnnl.gov

Thank you

Pacific Northwest
NATIONAL LABORATORY

We value your feedback!

https://www.surveymonkey.com/r/PNNL042021

Join us for these upcoming webinars

Catalysis - Nature's Way
Bojana Ginovska
April 27, 2021 | 5:00 pm

Improving Environmental Monitoring, Reducing Stressors, and Getting Marine Renewable Energy Devices into the Water
Alicia Amerson
May 11, 2021 | 5:00 pm

Talking Trash: Finding the Value in Plastic Waste Through Chemical Upcycling
Lily Hale
June 8, 2021 | 5:00 pm