

# Safety Risks and Risk Mitigation - Battery Energy Storage Systems

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## **Electrochemical Safety** Research Institute (ESRI)

Advancing the development of safer energy storage and energy generation through science

Novel **Materials** and New Energy Forms

Safety Research

Outreach

and **Standards** 

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### Introduction

- Energy storage in the form of batteries has grown exponentially in the past three decades.
- Batteries have been used in various consumer and unique applications for more than 70 years consumer, space, DoD (Army, Navy, AirForce), DOE, etc.
- Lithium-ion batteries are used in most applications ranging from consumer electronics to electric vehicles and grid energy storage systems as well as marine and space applications.
- Apart from Li-ion battery chemistry, there are several potential chemistries that can be used for stationary grid energy storage applications.
- A discussion on the chemistry and potential risks will be provided.
- Challenges for any large energy storage system installation, use and maintenance include training in the area of battery fire safety which includes the need to understand basic battery chemistry, safety limits, maintenance, off-nominal behavior, fire and smoke characteristics, fire fighting techniques, stranded energy, de-energizing batteries for safety, and safely disposing battery after its life or after an incident.



## **Aqueous Zinc-Ion Battery**





- Self charging (air from ambient environment)
- C/3 rate
- Theoretically capable of high discharge rates
- At 100C rate, 1/5<sup>th</sup> of C/3 rate capacity is obtained
- 10,000 cycles



## **Aqueous Zinc-Ion Battery**



#### EOS

Conductive plastic anodes and carbon-felt cathodes

Aqueous electrolyte with blend of water, halides, additives, and buffering agents

Injection-molded thermoplastic polymer exterior



Organic Cathodes



Grignon, Eloi et al. iScience, Volume 25, Issue 5, 104204



## **Aqueous Zinc-Ion Battery**

### **Advantages**

- Simplicity of synthesis Zn is not sensitive to ambient environments
- Use of aqueous electrolytes higher ionic conductivity; near neutral pH (slightly acidic)
- Long-term stability
- Low cost (less expensive due to nature of materials used such as Zn and aqueous solvents)
- Higher level of safety compared to battery chemistries that use an organic solvent electrolyte such as Li-ion – with use of aqueous electrolyte
- More sustainable alternative (expected to have a lower carbon footprint)
- Environmentally friendly

### Disadvantages

Poor cycle life and low coulombic efficiency
Zn dendrite growth
Water break down that passivates or insulates the cathode surface
Corrosion of electrodes
Byproducts that are irreversible
Poor structural stability
Slow Electrode kinetics
Small working voltage range due to narrow

electrochemical stability window



### **Redox Flow Batteries**

• ESRI research team focused on two chemistries:

Zinc-Bromine RFB and Vanadium RFB.

• Both types of RFBs were evaluated for the safety at the system level under off-nominal conditions, such as overcharge, overdischarge, and external short circuit. The results of the studies for both systems will be presented.



### **Zinc-Bromine Redox Flow Battery**



A complexing agent such as MEP (N-methyl N-ethyl pyrrolidinium bromide) is added to the electrolyte to sequester bromine and prevent it from going into

the vapor phase



Judy Jeevarajan, Ph.D. / UL Research Institutes

• Positive electrode reaction:

$$2Br^{-} \stackrel{Charge}{\underset{Discharge}{\leftarrow}} Br_{2} + 2e^{-}$$

• Negative electrode reaction:

• Overall cell reaction:

$$ZnBr_2 \xrightarrow{Charge} Zn + Br_2$$
  
Discharge

## **Zn- Br : Overcharge Test: Gas formation**

 Reddish brown Br<sub>2</sub> gas reached the upper sensor limit (5 ppm)





## **Zinc-Bromine Flow Batteries**

#### **Advantages**

•Low cost: ZBFBs are inexpensive compared to lithium-ion batteries

- •Higher energy density- than other redox flow battery systems
- •Deep discharge capability: ZBFBs can be deeply discharged even down to 0 V.
- •Scalable and flexible: ZBFBs are scalable and flexible

### Disadvantages

•Low cycle efficiency: Typically around 70-80%, compared to lithium-ion batteries, which are usually 98% or higher

•Dendrite formation: Dendrites can form on the zinc anode, which can decrease battery efficiency, cause short circuits, and lead to battery fires

Material corrosion: Materials in ZBFBs can corrode
Short cycle life: ZBFBs have a short cycle life compared to liion, NiMH etc.

Low power density: Not capable of high-rate discharges
Toxicity: Presence of bromine and the release of bromine under off-nominal conditions are a toxicity concern

## Vanadium Redox Flow Battery (VRFB)



Positive electrode reaction:

 $\begin{array}{c} \text{Charge} \\ \text{VO}^{2+} + \text{H}_2 \text{O} \overleftrightarrow{\overset{}\leftarrow} \text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \\ \text{Discharge} \end{array}$ 

### Negative electrode reaction:

 $V^{3+} + e^{-} \mathop{\overrightarrow{\leftarrow}}_{\text{Discharge}} V^{2+}$ 

VRFBs consist of liquid electrolytes containing one or more vanadium electroactive species.

Vanadium - Oxidation States

Overall cell reaction: Charge  $V^{3+} + VO^{2+} + H_2O \rightleftharpoons VO_2^+ + V^{2+} + 2H^+$ Discharge



Courtesy: Dr. Daniel Juarez-Robles (SwRI) Judy Jeevarajan, Ph.D. / UL Research Institutes

## Vanadium Redox Flow Battery (VRFB) – Lab Scale



### Assembly of the Flow Cell

#### VRFB built at ESRI





## Vanadium Redox Flow Battery (VRFB)

### Advantages

•Long lifespan: VRFBs can last 50–100 years and are engineered to last 25 years even in demanding applications.

•Safety: VRFBs are non-flammable.

•Limited self-discharge: VRFBs have limited selfdischarge, making them useful for long-term storage

•Rapid response times: VRFBs have rapid response times (0.001 to 0.02 secs), making them well-suited for UPS applications
•Energy Efficiency: Up to 70%

#### Disadvantages

•High capital cost: VRFBs have a high capital cost. •Low power density: VRFBs have a relatively low power density (800 W/h).

•Toxicity: VRFBs are relatively toxic due to the oxides of vanadium.

•Weight: VRFBs are heavy due to the large electrolyte tanks and aqueous electrolyte (40 Wh/kg).

•Energy-to-volume ratio: VRFBs have a relatively poor energy-to-volume ratio (15-20 Wh/L).

•System complexity: VRFBs are more complex than standard storage batteries.



### **Iron Chloride Flow Battery**







https://iopscience.iop.org/article/10.1149/2.0161601jes/pdf



### **Iron-Chromium Flow Batteries**



https://www.battery.associates/

### **Iron Flow Batteries**

### **Advantages**

•Non-toxic and non-flammable: only slightly

reactive with water and air.

•Low-cost materials: materials are inexpensive, earth-abundant

•Long cycle life: Iron flow batteries have a theoretically unlimited cycle life (practical 10,000 cycles).

Sustainable: Iron flow batteries have a low lifecycle carbon footprint and substantially recyclable or reusable at the end of their life.
20 year life

•Rapid response: Can help with frequency control on the grid

### Disadvantages

•Low round-trip energy efficiency: A competitive side reaction at the negative electrode during charging causes low round-trip energy efficiency.
•Low cell voltage: Iron flow batteries have a low cell voltage (1.2 V).
•Hydrogen evolution: Hydrogen evolution can occur during charging (operate below pH 3.5).
•Low Electrochemical Performance: Iron chloride flow batteries have low charging efficiency, self-discharge.

•Large size: may not be suitable for residential use

### **Iron Air Batteries**



METALLIC Iron

AIR

DISCHARGE

RUST

Research Institutes



https://nanografi.com/

## **Iron-Air Batteries**

#### Advantages

•Cost-effective: Iron-air batteries are less expensive than lithium-ion batteries, especially for large-scale energy storage.

•Environmentally friendly: Iron-air batteries use non-toxic, abundant materials and are recyclable.

•Long-duration storage: Iron-air batteries can store energy for days (up to 100 hours), which is ideal for balancing renewable energy sources like wind and solar.

•Safe: Iron-air batteries are safer than lithium-ion batteries because they use non-flammable materials and are less likely to overheat.

High energy density: Iron-air batteries have a higher energy density than many traditional flow batteries.
Modular and scalable

#### Disadvantages

•Slow to charge and discharge: Iron-air batteries are slower to charge and discharge than lithium-ion batteries, making them less suitable for laptops or smartphones.

•Size and weight: Iron-air batteries are larger and heavier than lithium-ion batteries.

•Air electrode stability: The stability of the air electrode is not yet sufficient for use as a stationary storage device.

•Scale up and Cycle Life: Scaling up production and improving the durability and cycle life of the batteries are challenges (theoretical cycle life is 10,000 cycles/ 30 years)

## **Zinc- Air Rechargeable Batteries**



Research nstitutes



Specific energy	470 (practical),1370 (theoretical) <u>Wh/kg</u>
Energy density	1480-9780 <u>Wh</u> / <u>L</u>
Specific power	100 <u>W/kg</u>
Nominal cell voltage	1.45 <u>V</u>

## **Zinc- Air Rechargeable Batteries**

### Advantages

•**Cost-effective**: Zinc is abundant, making zinc-air batteries inexpensive.

•Environmental: Zinc-air batteries have a low environmental impact.

•Energy density: Zinc-air batteries have a high volumetric energy density, meaning they provide more energy for their size than conventional batteries.

•Safety: Zinc-air batteries are safer than lithiumion batteries because they have chemically inert components and minimize fire risk.

•Shelf life: Zinc-air batteries have a long shelf life if sealed to keep air out.

### Disadvantages

•Limited output: Zinc-air batteries have a limited power output and short lifespan.

•Water loss: Zinc-air batteries lose water over time because they rely on atmospheric oxygen.

•Dendrite formation: Zinc dendrites can form on the anode, causing the cell to short and fail.

•Oxygen reduction reaction: The oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics are sluggish, which hinders commercialization.

•Air electrode corrosion: The air electrode can corrode.

## Factors to Consider in Installation of Chargers / Charging Infrastructure Inside Buildings

- Ventilation
- Toxic gas sensors
- Oxygen sensors

- Currently available commercial sensors installed inside ESS containers are overwhelmed; first responders are recommended to carry their own gas sensors when entering such enclosed areas that can trap toxic and combustible gases
- Access to charging station main power
- Access to charging station / battery data (Battery Management System) – to determine stranded energy and reignition concerns)
- Physical access for first responders and fire fighters
- Proper PPE/ respirators (acid gas for Li-ion battery fires)
- Relevant fire extinguishers

## **Challenges for Energy Storage Systems**

Toxicity (of vented liquids and gases)	
Flammability and Off-gassing	
Environmental Pollution	
High Voltage Safety	
Vent products - particulates	
Fire Extinguishing methods	
Transportation Safety	

### **BESS Procurement Certification**





### **Areas of Bottlenecks in BESS for Authorities and Operators**





### **Standards and Regulations Relevant to the BESS Maintenance**



### **Codes, Standards Relevant to the BESS Fire Detection and Safety**





## **Standards and Regulations Relevant to the BESS Operation**



## **Summary**

- Few non-Lithium-ion battery chemistries are either in existence and several in research or small scale.
- Vanadium redox flow batteries are the oldest with some dating back to the 1860s (Schmid Group, Germany)
- A full characterization (from cell to battery to entire system) to understand the limitations with respect to safety should be carried out.
- Certifications based on standards should be completed at the battery as well as entire system level.
- Attention should be paid to limitations of the systems that are related to fire, smoke, toxicity, and environmental pollution.
- Maintenance and periodic audits are imperative for safe functioning of longterm energy storage installations.

# **Back-up Slides**

### References

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