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Characterization of Safety for Two Flow Battery Chemistries

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Discoveries in Safety™

Introduction

- The Electrochemical Safety Research Institute (ESRI) has carried out research in the area of redox flow batteries (RFBs).
- The objective is to study the electrochemical and safety aspects of RFBs to help in setting the relevant standards.
- 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, over-discharge, and external short circuit. The results of the studies for both systems will be presented.

$$ZnBr_2 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} Zn + Br_2$$

$$V^{3+} + VO^{2+} + H_2O \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} VO_2^{+} + V^{2+} + 2H^{+}$$

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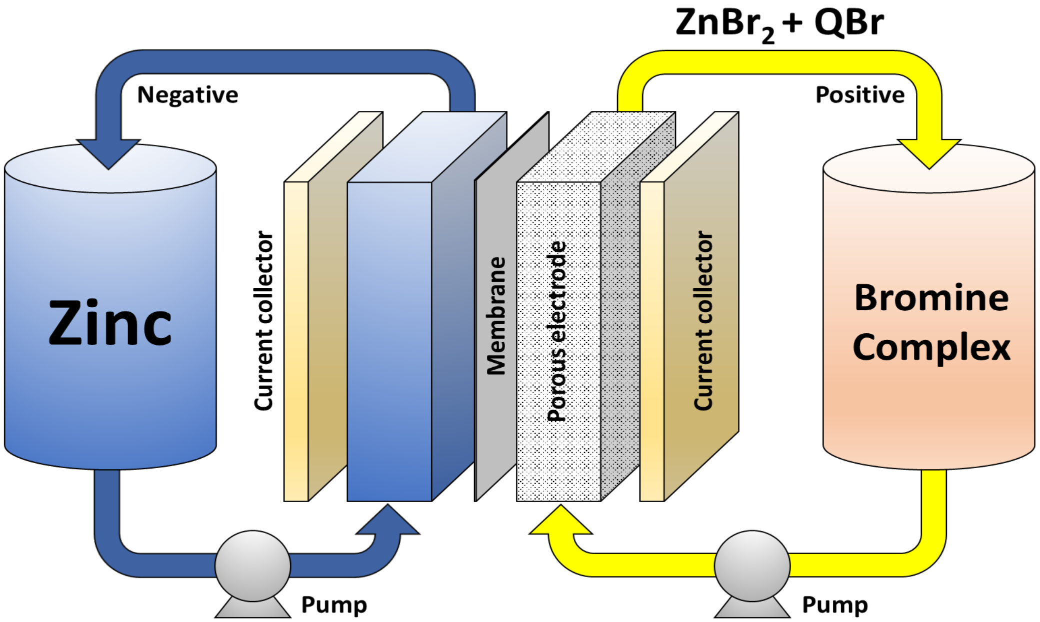
Zinc-Bromine RFB

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

- Positive electrode reaction:

$$2Br^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} Br_2 + 2e^-$$

- Negative electrode reaction:

$$Zn^{2+} + 2e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} Zn$$

- Overall cell reaction:

$$ZnBr_2 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} Zn + Br_2$$

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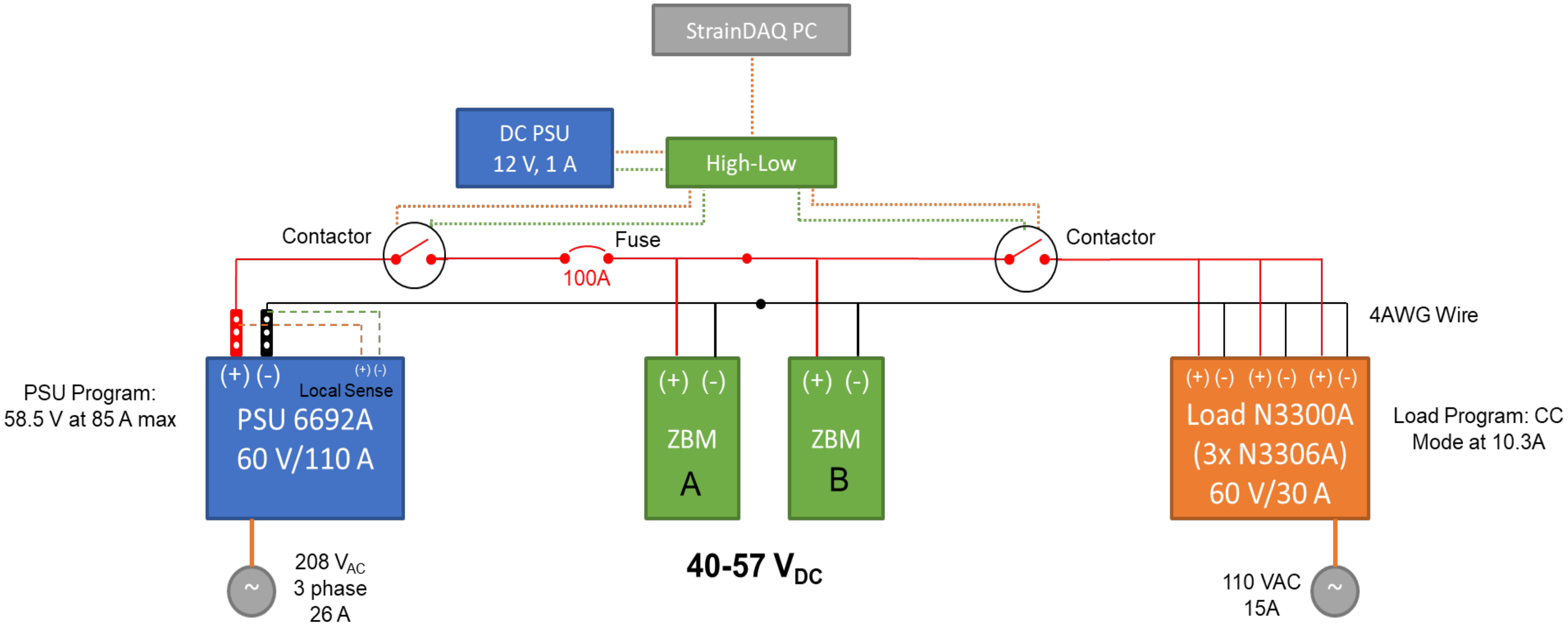
Zn-Br Flow Battery Wiring Diagram



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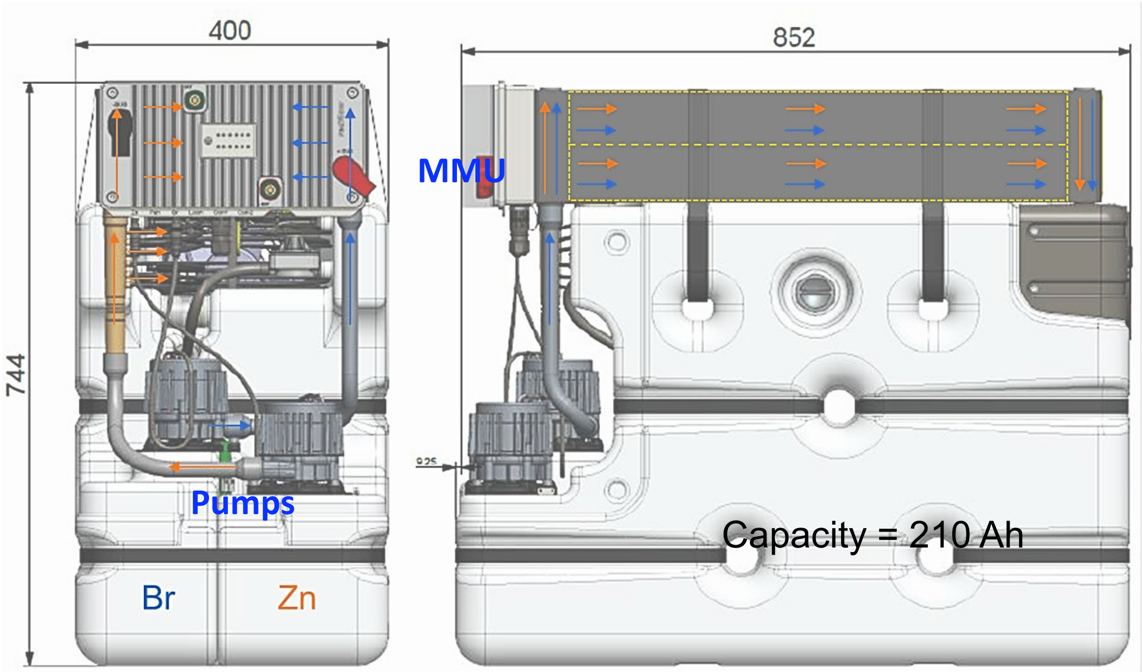
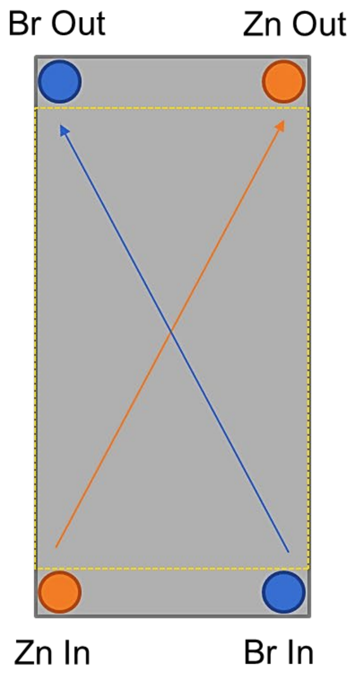
Zn-Br Test Battery Design Schematic



Courtesy: Redflow

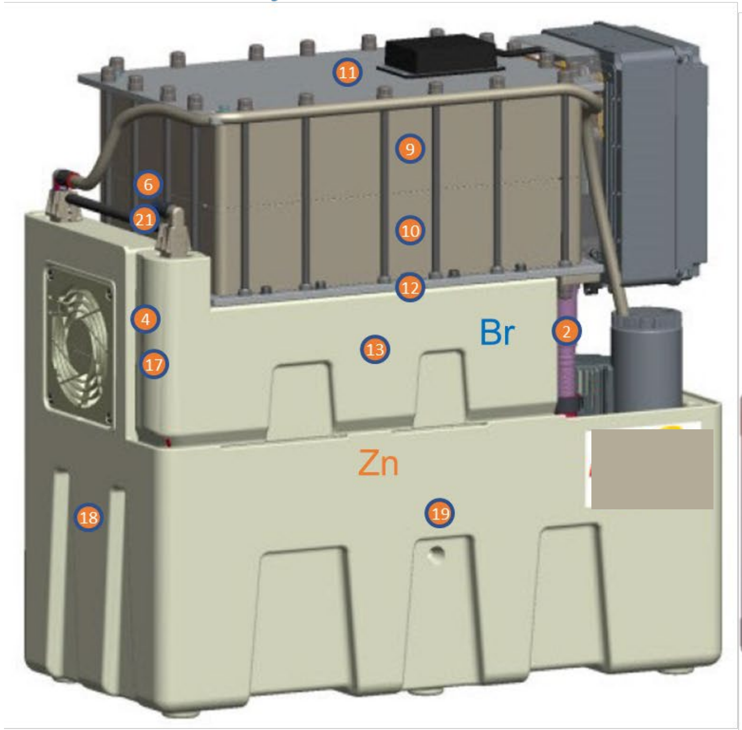


Module management unit (**MMU**) is designed to prevent unsafe operation.

- 10 kWh Battery, **E = 40 - 57 V**
- Cycle life = **3650 cycles** (10 years)
- 100 liters of water-based solution of zinc-bromide
- 2 electrode stacks connected in parallel (1 stack = 30 cells in series)

Zn-Br Test Article: Location of thermocouples

TC Layout for Abuse



TC	Location
01	Br Pump Outlet
02	Zn Pump Outlet
03	Cooling Tubes Front
04	Cooling Tubes Rear
05	Electrode Stack Front
06	Electrode Stack Rear
07	Electrode Stack Side Left Top
08	Electrode Stack Side Left Bottom
09	Electrode Stack Side Right Top
10	Electrode Stack Side Right Bottom
11	Electrode Stack Top
12	Electrode Stack Bottom
13	Br Tank Side
14	Zn Tank Side
15	Br Tank Front
16	Zn Tank Front
17	Br Tank Rear
18	Zn Tank Rear
19	Zn Tank Side
20	Ambient 1
21	Vent
22	Ambient 2
V	Battery Voltage
I	Current

Zn- Br Flow Battery Test Plan: Abuse Tests and Cycle Life

Overcharge Test

- Carried out on a fully charged battery
- CC charge at 45 A to a limit of 100 V or until a total of 600 Ah of capacity was achieved

Notes:

Module Management System needs to be bypassed to perform the overcharge test

External Short

- Carried out on a fully charged battery
- External short with a shunt resistance less than 20 mohms held for a minimum of 3 hours

Notes:

Abuse test requires cables capable of withstanding large currents, MMS bypassed

Overdischarge

- Battery is fully charged first
- CC discharge at 30 A to 0.0 V
- Remove 150% of the nominal capacity after reaching 0 V

Notes:

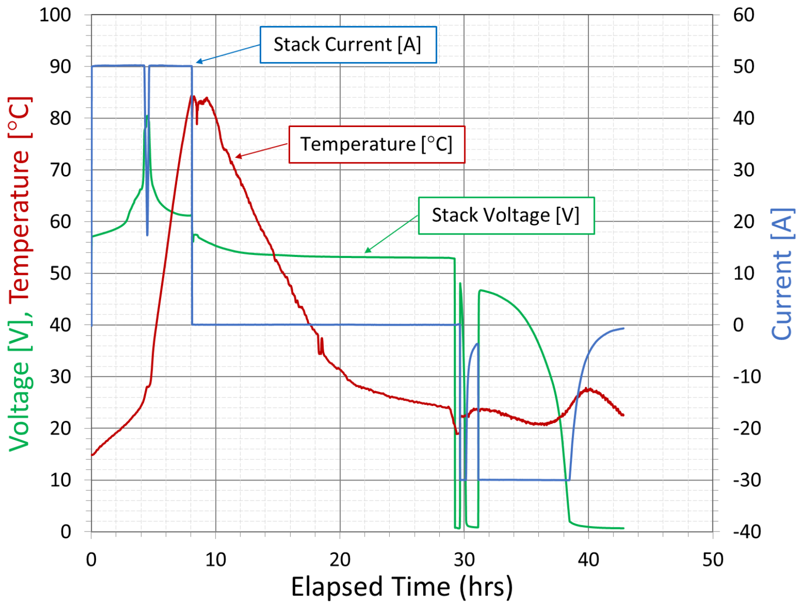
- Battery can be overdischarged without any observable hazards, MMS bypassed

Cycle-life

- CC charge at 42.5 A to 58.5 V; CC discharge at 42.5 A to 0 V. Total: 100 cycles
- One maintenance cycle performed every 72 hours (by internally running the pumps to discharge stack to 0 V and lets it sit for ~3 hours.

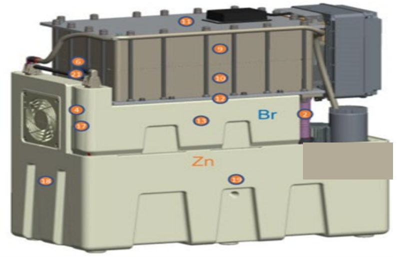
Note: pH and conductivity measurements for catholyte and anolyte were carried out after each abuse test

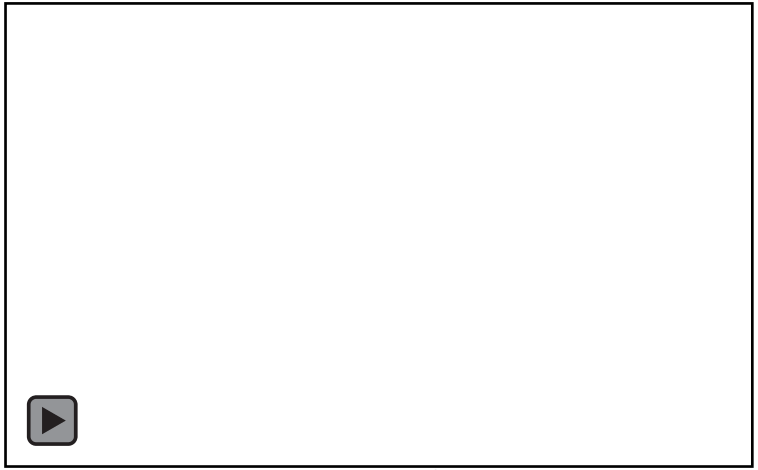
Zn- Br : Overcharge Test



45 A charge with a limit of 100 V or a total of 600 Ah

Thermocouple 4



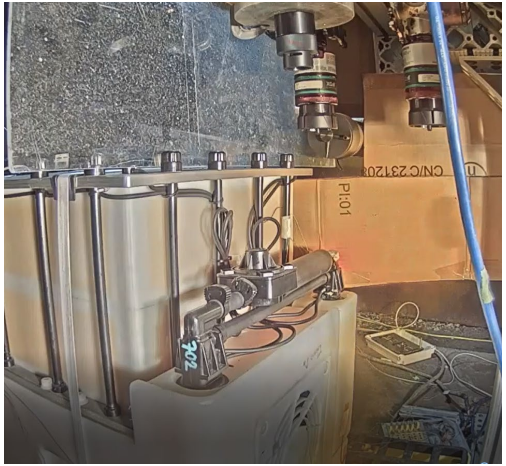


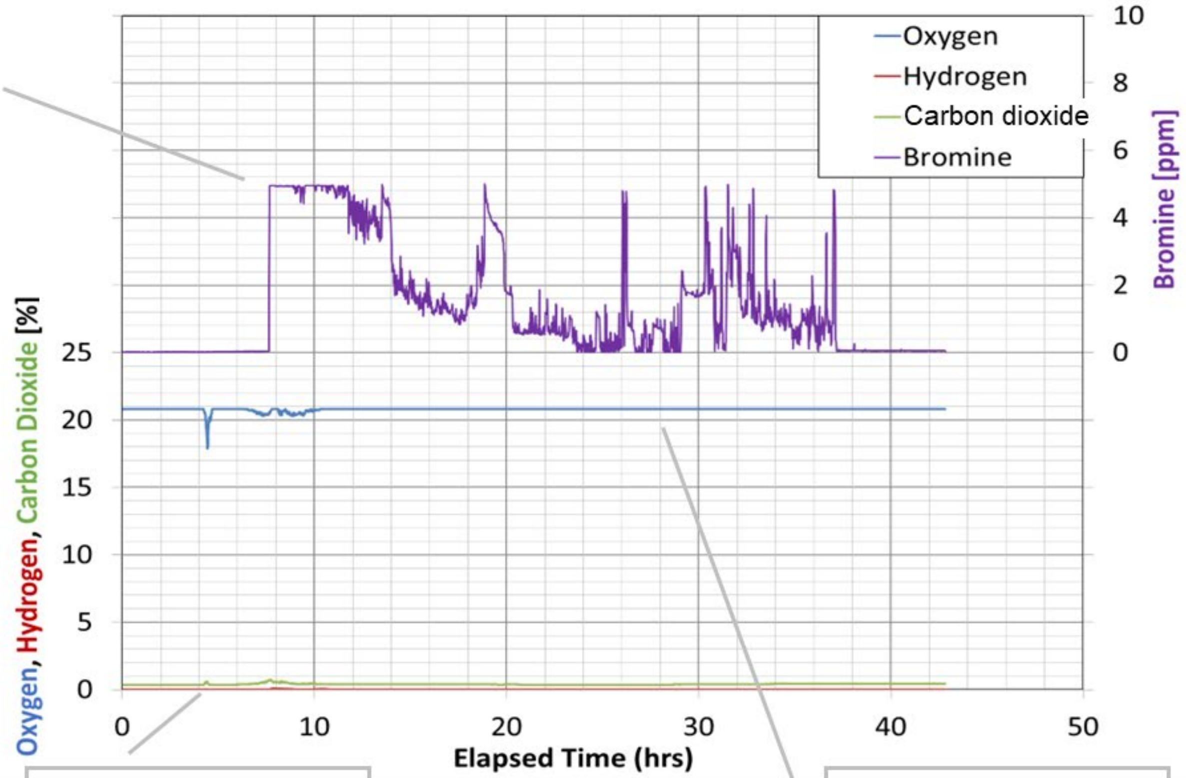
<u>During the overcharge test,</u>

- **Gaseous bromine formation increased**
- **Temperature reached to ~83 °C at the catholyte tank (TC-04) prior to the release of Br_2 (g)**
- **The electrolyte tank was slightly deformed after the overcharge test.**

Zn- Br : Overcharge Test: Gas formation

- Reddish brown Br_2 gas reached the upper sensor limit (5 ppm)



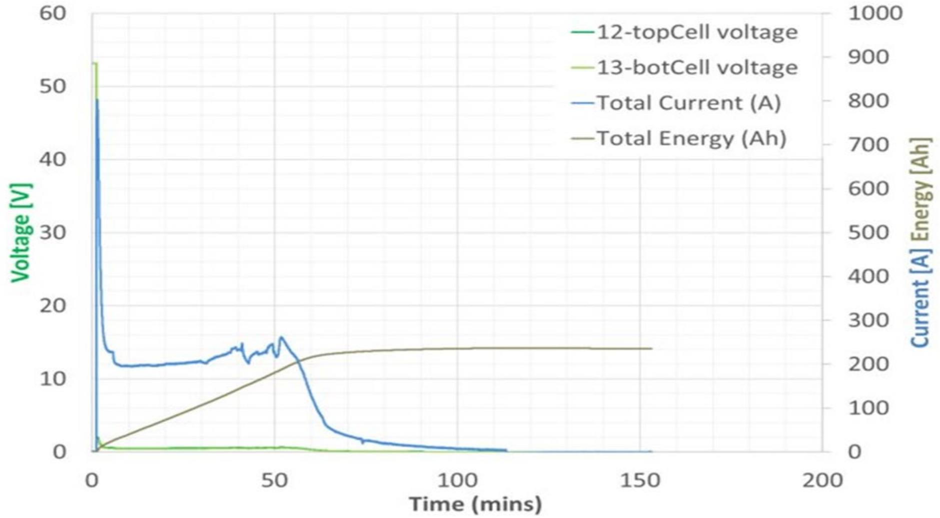


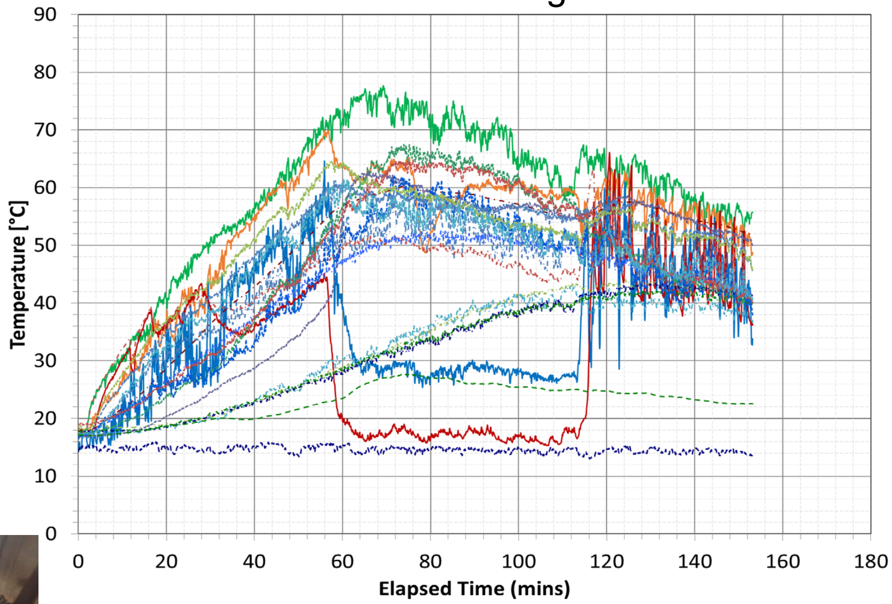
H_2 & CO_2 (~0%)

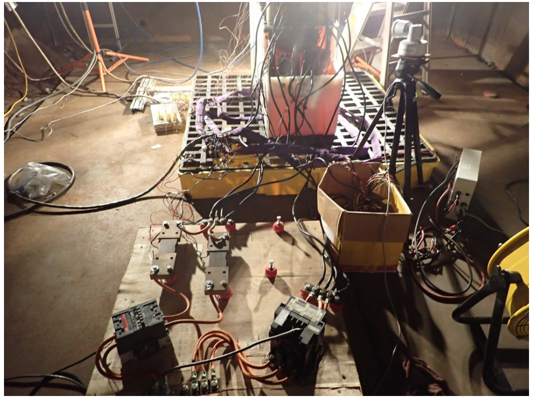
O_2 in air (21%)

Zn- Br : External Short Circuit

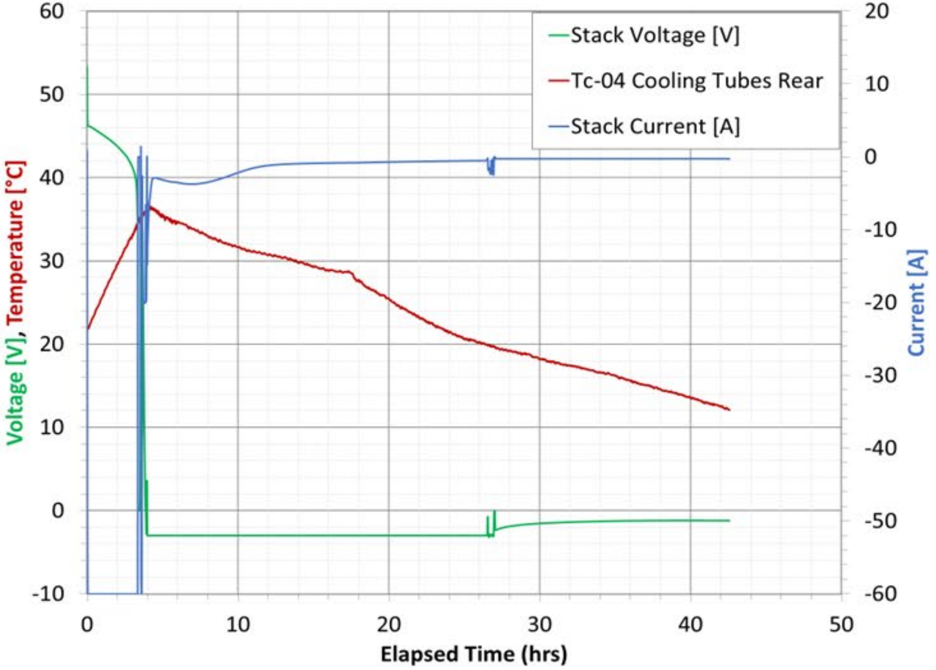
Load of ~20 mohms and held for 3 hours or until voltage falls to 0 V

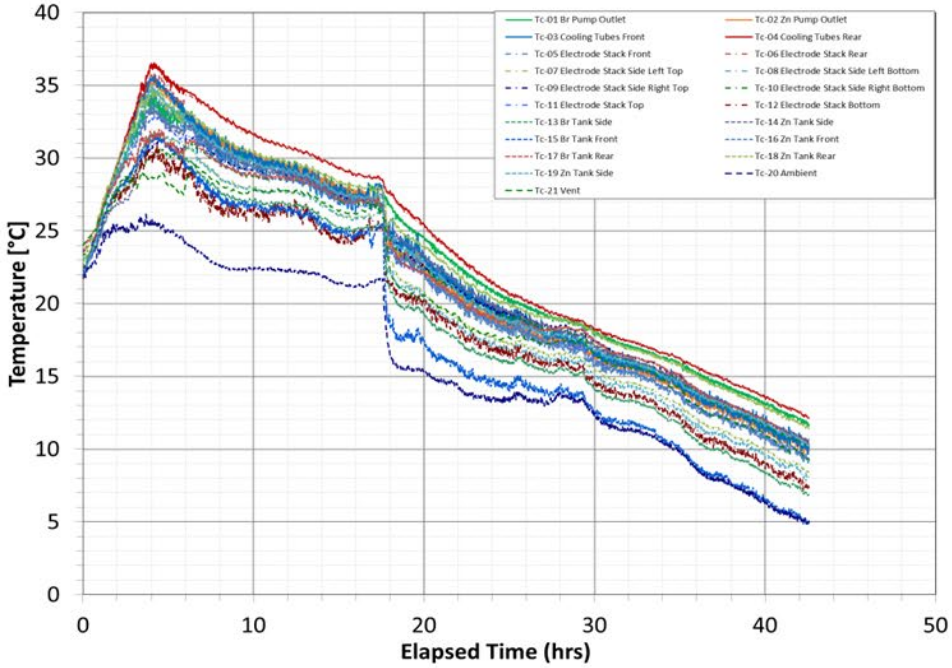






Zn- Br : Overdischarge Test





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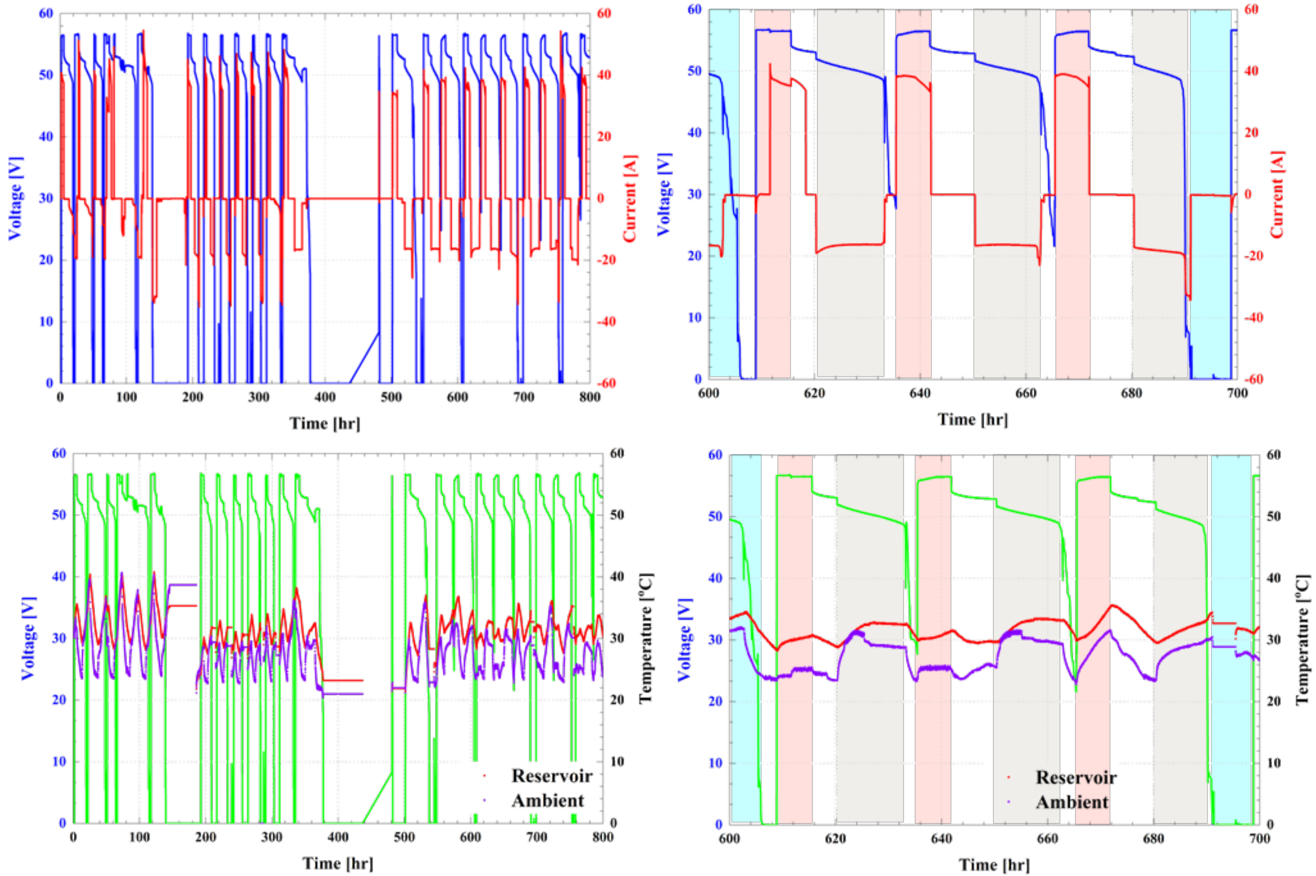
Zn-Br : Cycle Life Studies



Cycling Protocol

- Current = 42.5 A
- Voltage = 58.5 V
- 8 hr charge
- 14 hr discharge

Maintenance cycle:

- Discharge to 0.0 V (0% SOC)
- Recover plated zinc
- 3 hours

100 cycles in 3 months

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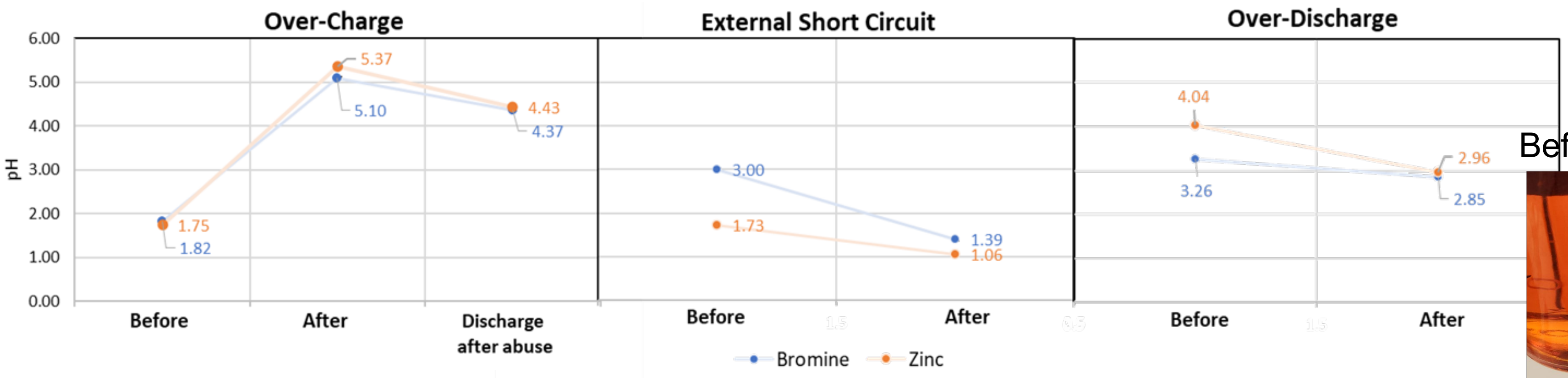
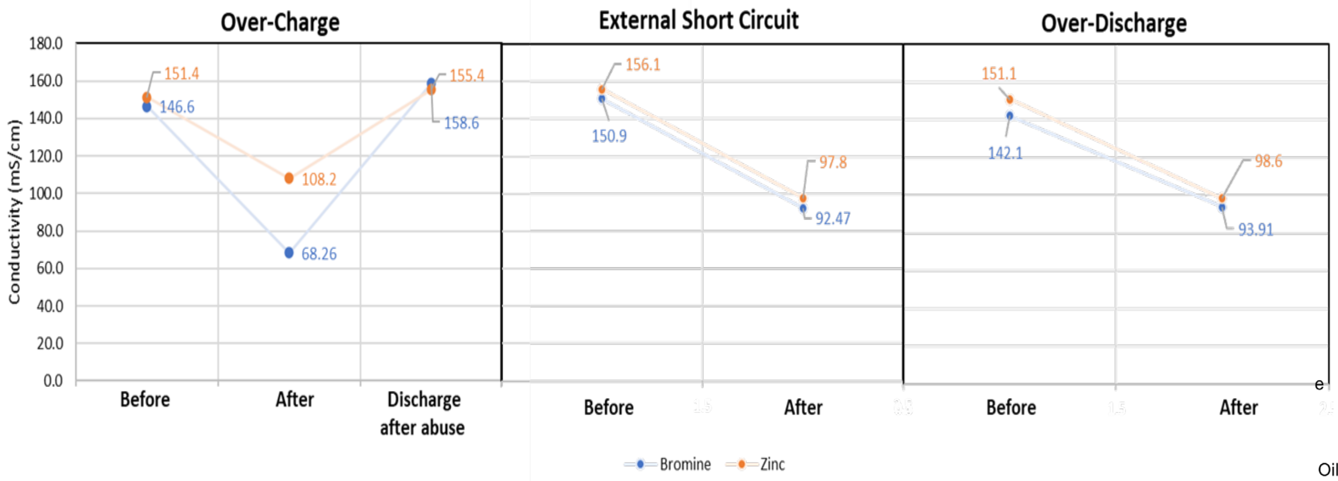
Zn- Br : Electrolyte Analysis: pH and conductivity measurements



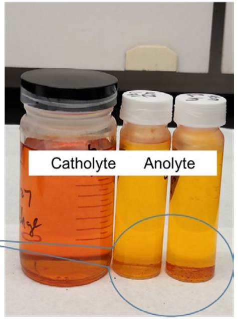


Before Test

Clear solution in catholyte

After Test

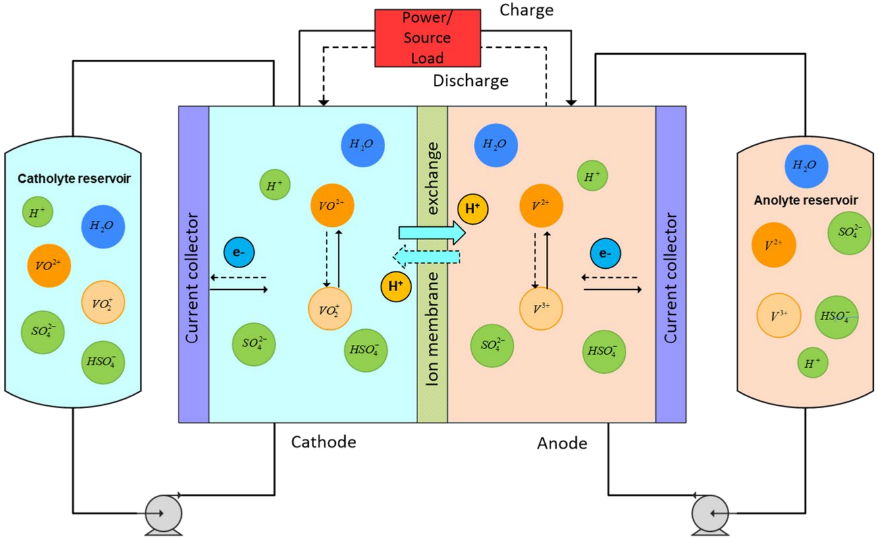
Oily product is observed in the anolyte (discharged sample after overcharge test)



Discharge after abuse

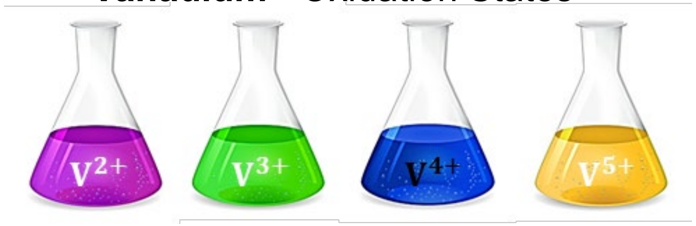
Vanadium Flow Battery

Vanadium Redox Flow Battery (VRFB) – Lab Scale



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

Vanadium - Oxidation States



Courtesy: Dr. Daniel Juarez-Robles (SwRI)

Positive electrode reaction:

$$VO^{2+} + H_2O \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} VO_2^{+} + 2H^{+} + e^{-}$$

Negative electrode reaction:

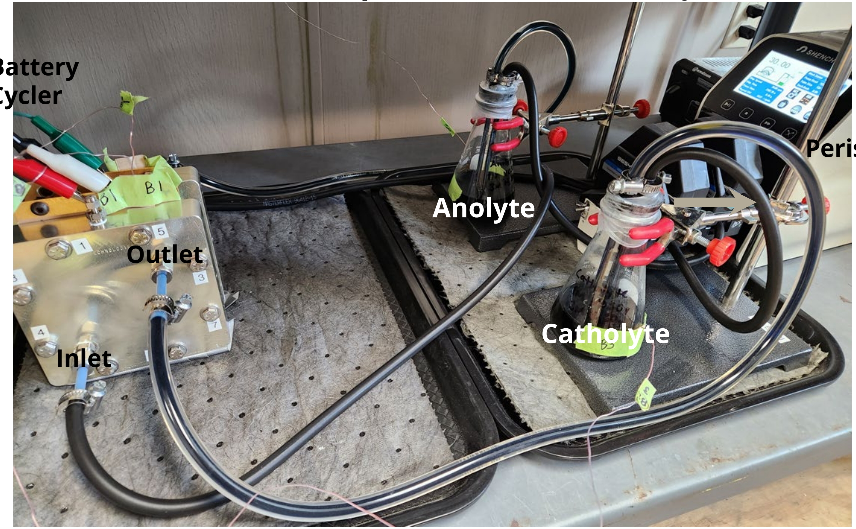
$$V^{3+} + e^{-} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} V^{2+}$$

Overall cell reaction:

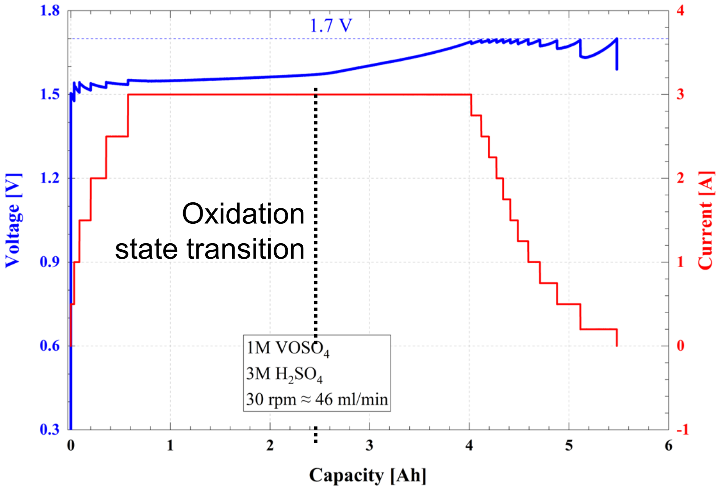
$$V^{3+} + VO^{2+} + H_2O \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} VO_2^{+} + V^{2+} + 2H^{+}$$

VRFB - Experimental Setup

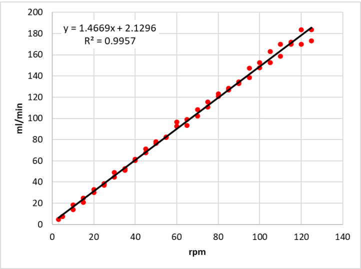
Test Setup - Lab scale Battery



Electrolyte Pre-charge



Pump flow rate



Electrochemically active area
A = 50 cm²

Nafion 212

- 50.8 µm, 0.10 S/cm

Sigracell Carbon Felt

- 2.5 mm Thickness
- 90% Porosity
- BET Surface Area = 0.4 m²/g

Anolyte

V^{4+} → V^{3+} → V^{2+}

Catholyte

V^{4+} → $V^{4+} + V^{5+}$ → V^{5+}

Catholyte volume = 2X Anolyte volume

Remove half the volume

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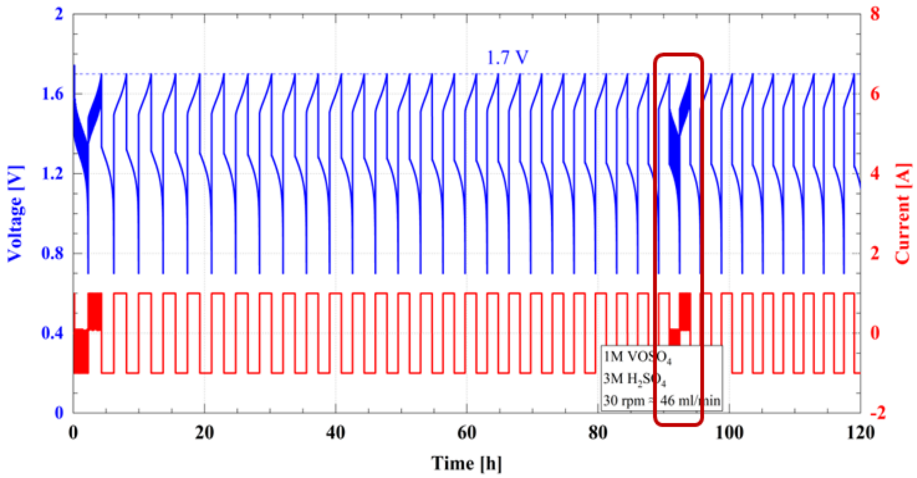
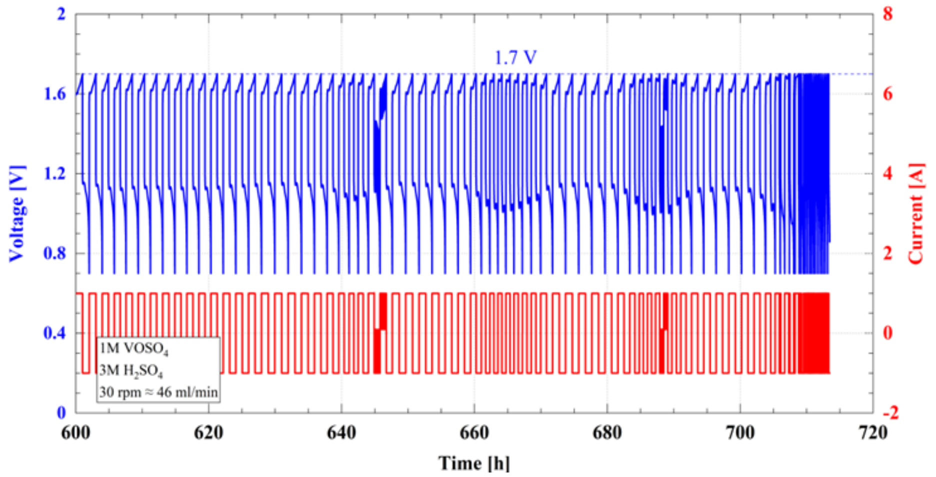
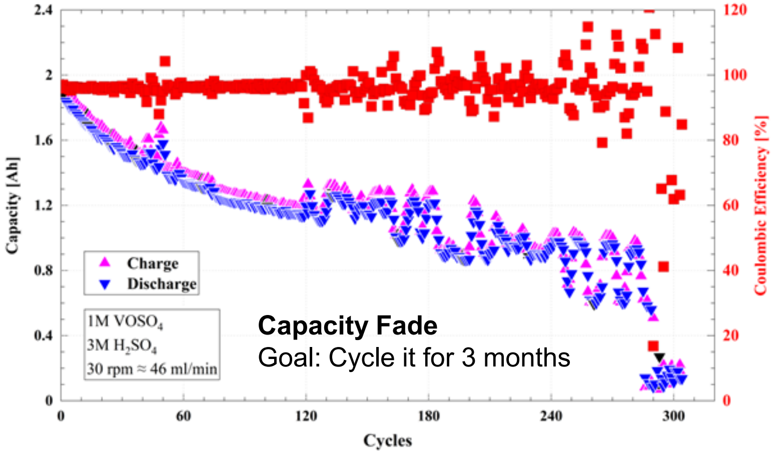
VRFB - Cycle Life Tests

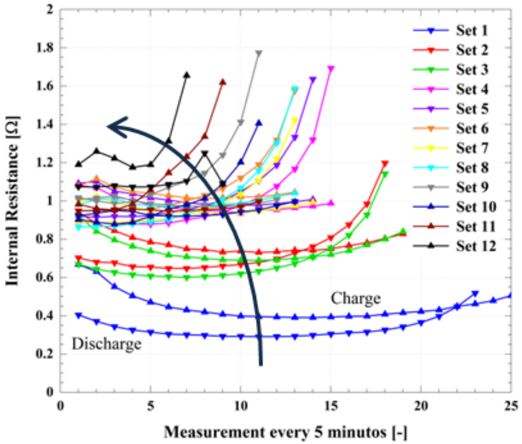






Capacity Fade

Goal: Cycle it for 3 months



Internal Resistance Measurement, **1.5C Pulse for 100 ms** every 5 minutes.

Resistance increases at the end of the discharge

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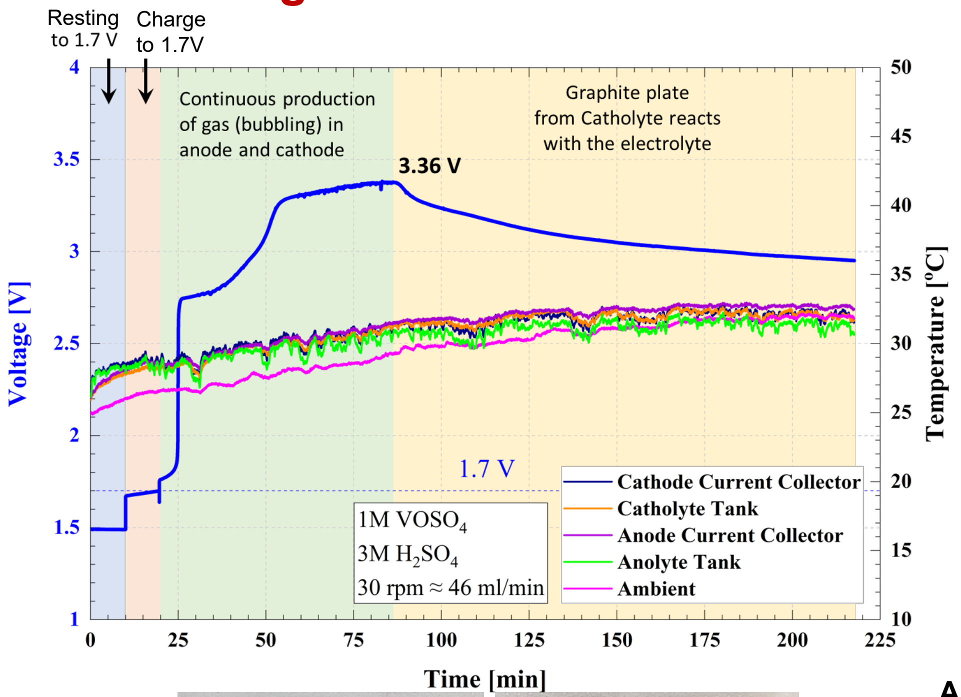
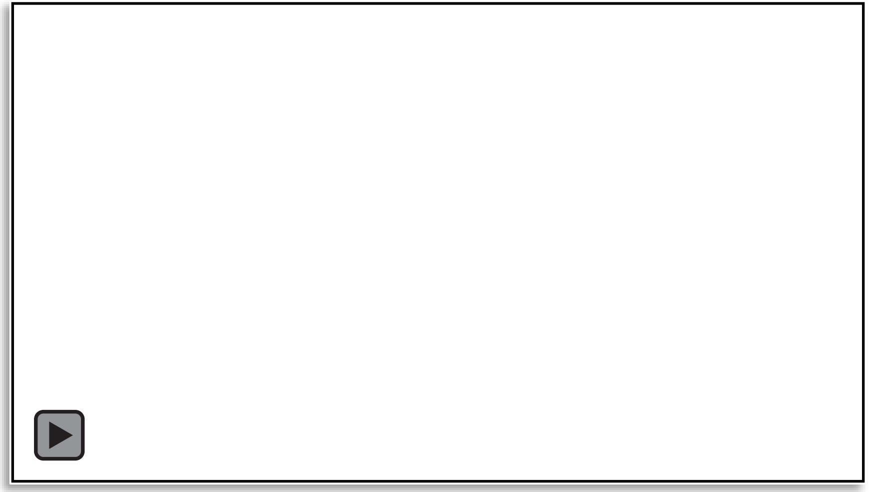
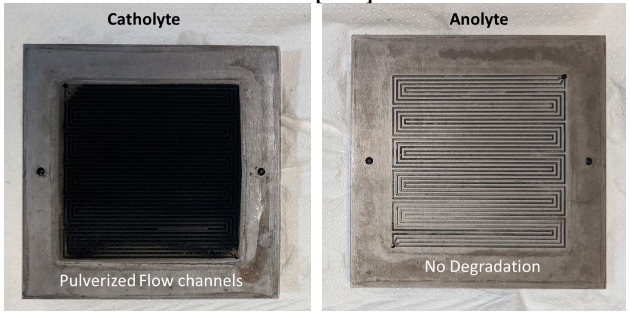
Overcharge – Lab-Scale Vanadium Flow Battery



Overcharge Test





Anolyte

V^{2+} → Potential decreases

Catholyte

V^{5+} → Potential increases

Gas Production

Composition?

$$VO^{2+} + H_2O \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2^{+} + 2H^{+} + e^{-}$$

$VO^{2+} \rightarrow V^{4+}$, $VO_2^{+} \rightarrow V^{5+}$

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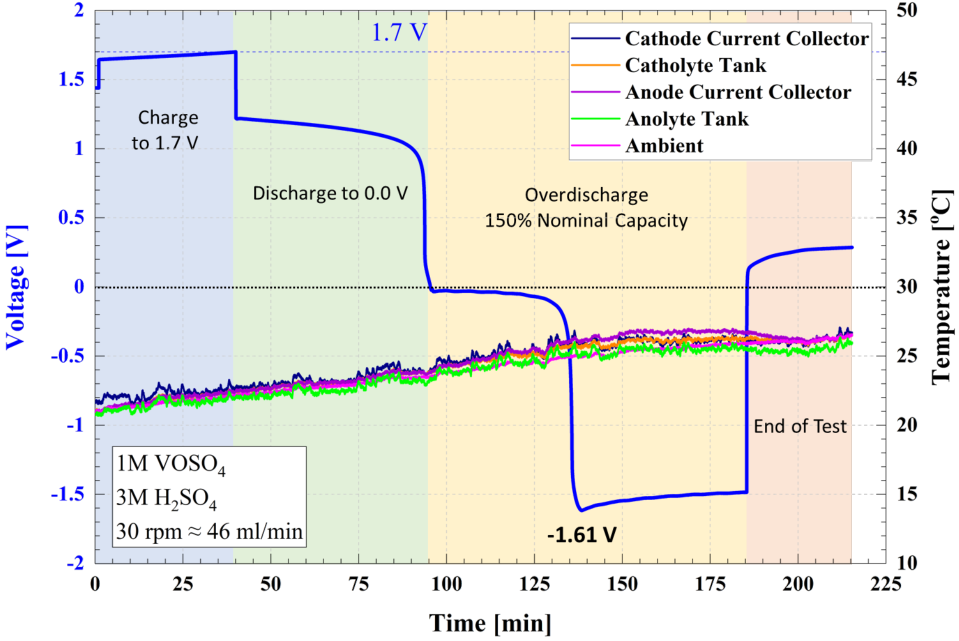
Overdischarge – Lab-Scale Vanadium Flow Battery



Overdischarge Test

No Bubbling Observed

Anolyte

V^{2+} → V^{3+} → V^{4+} ↛ V^{5+}

Catholyte

V^{5+} → V^{4+} → V^{3+} ↛ V^{2+}

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Summary

- Research studies typically characterize factors affecting flow battery performance but not the safety under off-nominal conditions.
  - If the electrolytes degrade or are used up, they can be replaced, thus restoring the battery capacity.
- It is usually assumed that the high heat capacity of the aqueous electrolyte can prevent temperature rise. However, the toxicity or flammability of the gases released, or the degradation and changes that occur to the flow battery components under off-nominal conditions have not been investigated.
- Flow batteries cannot be tested by just characterizing the flammability of the electrolytes. Safety tests appropriate to the credible off-nominal failure modes should be carried out at the system level to confirm safety of the batteries.

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Acknowledgments

- Electrochemical Safety Research Institute Team
Dr. Migo S. Ng (Zn-Br Abuse tests), Dr. Taina Rauhala (Lab-scale VRFB) and Dr. Judy Jeevarajan
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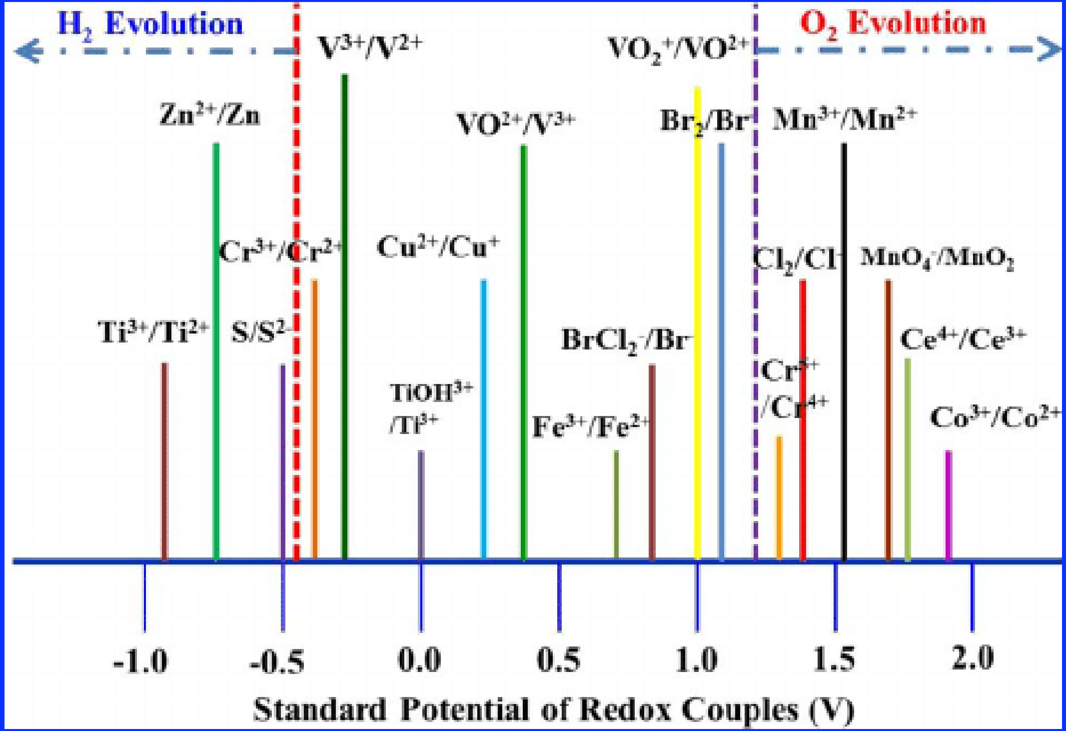
Carlos Lopez and Dr. Steve Kinyon

Dr. Daniel Juarez Robles currently with SwRI, for work on lab-scale flow batteries

Thank you!

[Backup Slide] Standard Potential vs. SHE

Charge | Discharge | Discharge | Charge



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