Pacific Northwest NATIONAL LABORATORY

2023 DOE OE Peer Review

Presentation ID #302

(Session 3: Safety & Reliability)

Reliability Investigation of All-Vanadium Redox Flow Batteries

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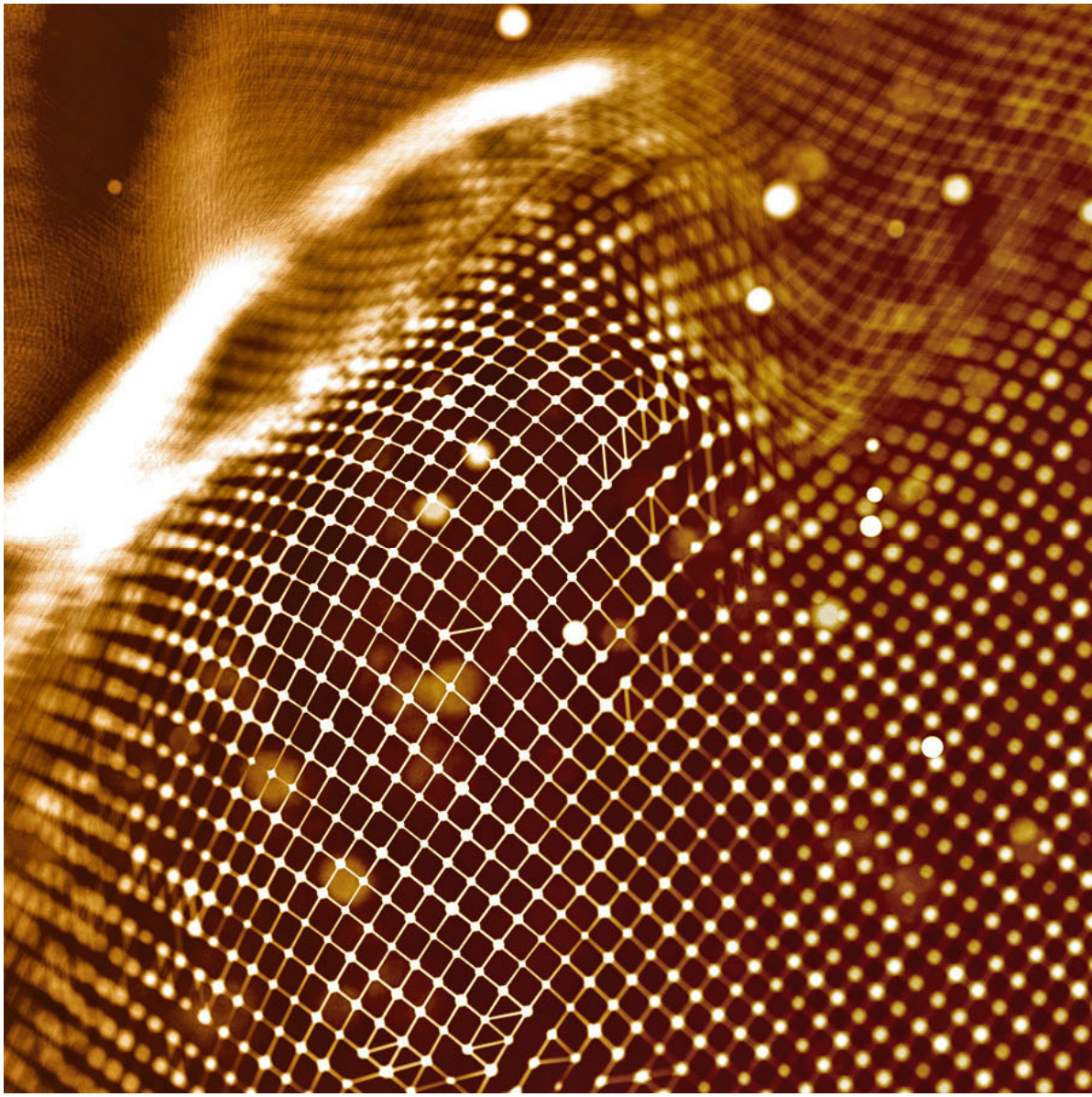

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2023.10.24

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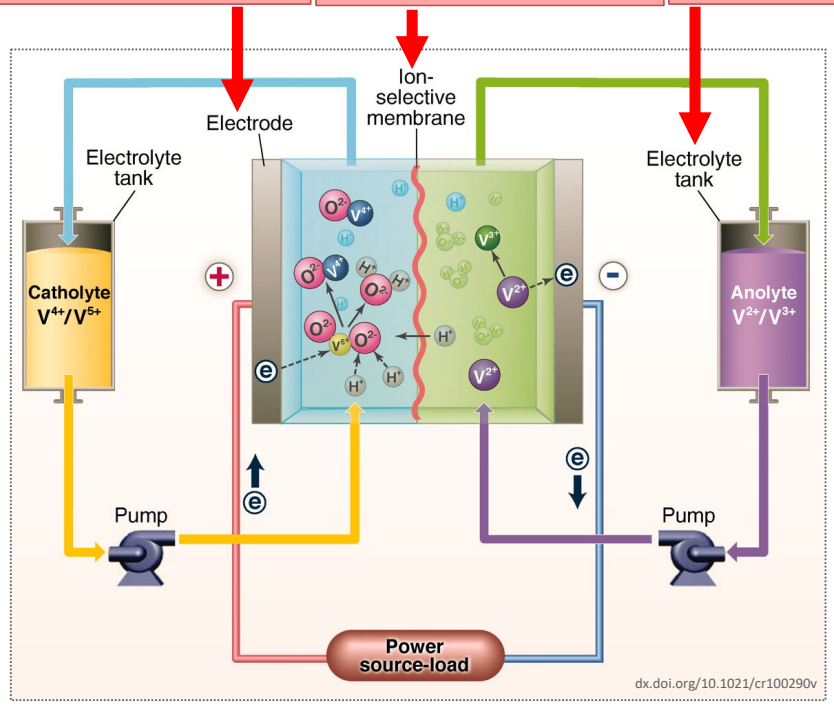
Outline

- **A Stable Reference Electrode Development**
  - Multi-Gen Development
  - Reliability Investigation by a Stable RE
- **Accelerated Stressor Lifetime Testing (ASLT) Protocols Development**
  - Testing Procedure Development
  - Stressor Study

Background: VRFB & Degradation Mechanisms

- **Carbon materials oxidation** (by electrolyte or high potential)
- **Electrolyte crossover**
- **Membrane degradation**
- **Electrolyte precipitation** (as a function of temperature)



- **Other components degradation** (bipolar plate, gasket, current collector)

***Challenges: Absence of a stable reference electrode and an accelerated testing protocol.**

Redox Flow Battery: Stationary Energy Storage

- Separation of energy capacity and power output
- High safety
- Long cycle life
- Ease of manufacturing

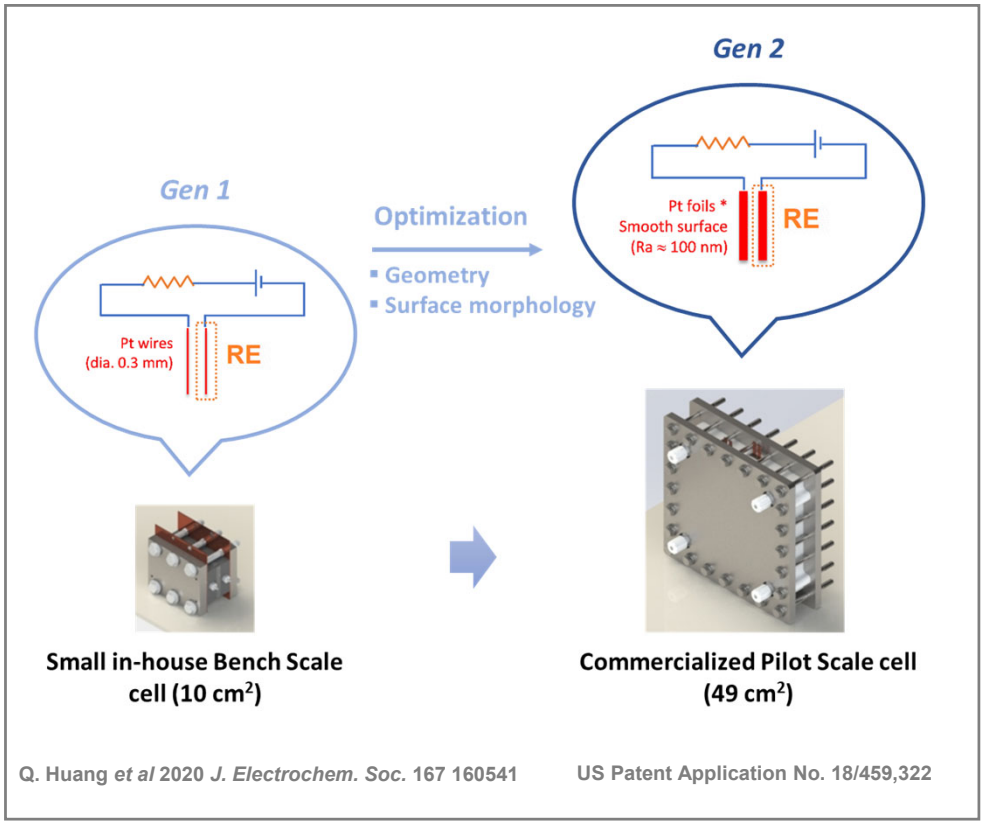
VRFB: Utilize four oxidation states of vanadium ions to form two soluble redox couples (VO^{2+}/VO_2^+ and V^{2+}/V^{3+}) as catholyte and anolyte.

Cathode:	$VO^{2+} + H_2O \leftrightarrow VO_2^+ + 2H^+ + e^-$	$\Delta E° = 1.00$ V
Anode:	$V^{3+} + e^- \leftrightarrow V^{2+}$	$\Delta E° = -0.25$ V
Full Cell:	$VO^{2+} + H_2O + V^{3+} \leftrightarrow VO_2^+ + V^{2+} + 2H^+$	$\Delta E° = 1.25$ V

One of the most mature redox flow technologies: high efficiencies and high electrochemical reversibility

I. A Stable Reference Electrode Development

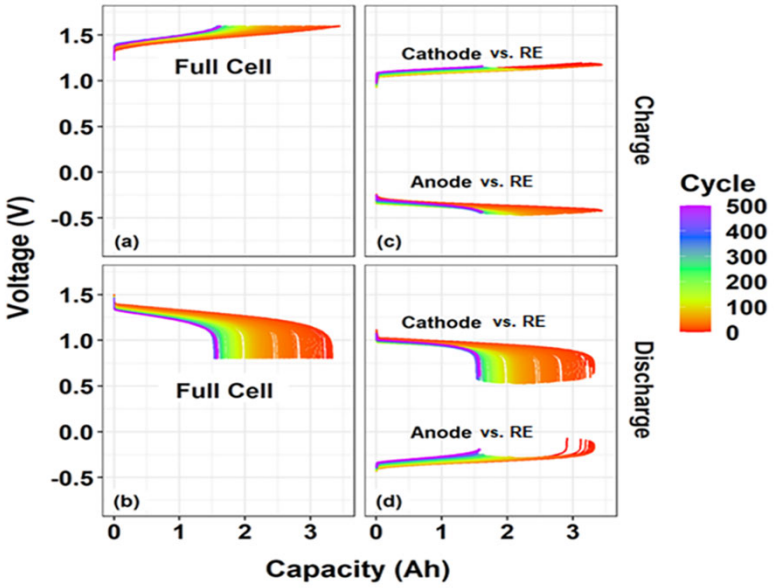
Multi-Gen Development



Q. Huang *et al* 2020 *J. Electrochem. Soc.* 167 160541

US Patent Application No. 18/459,322

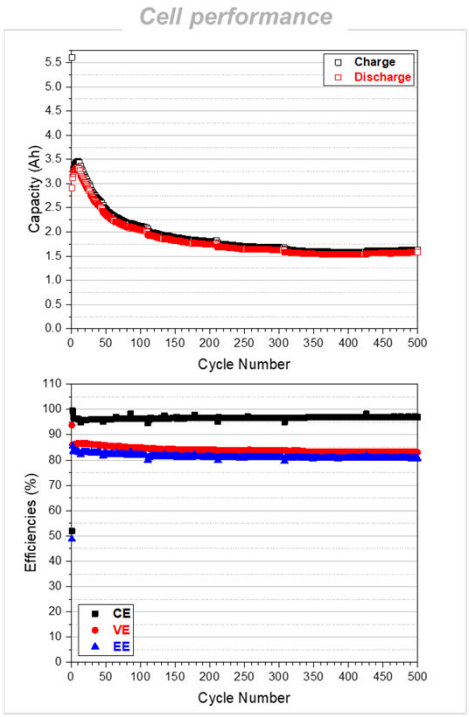
Ultra-Stable RE to Decouple Cathode & Anode

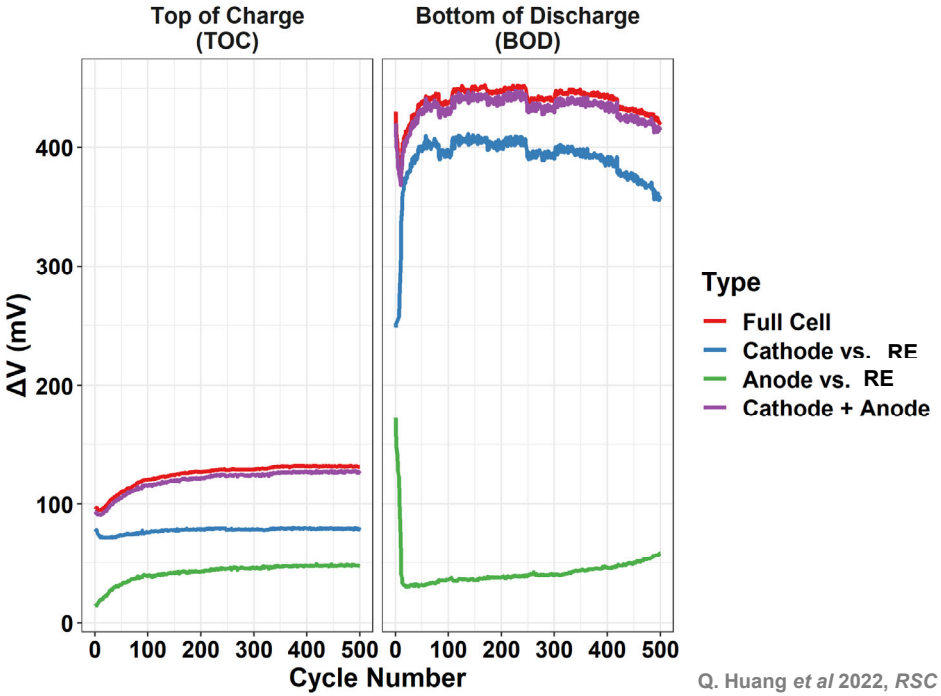


Performance degradation	Charge		Discharge	
	1st -100th	101st -500th	1st -100th	101st -500th
Individual electrode contribution	Anode	Anode	Cathode	Anode

Q. Huang *et al* 2022, *RSC Advances*,12, 32173

Reliability Investigation by a Stable RE: Overpotential



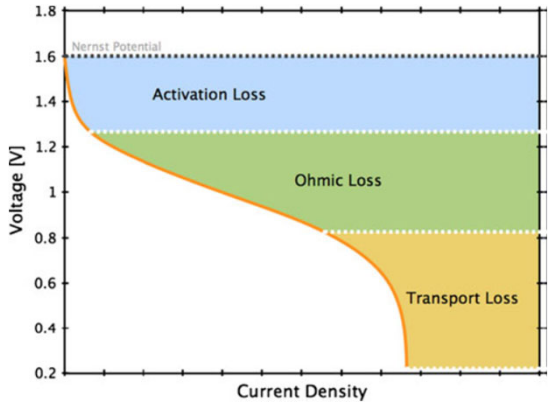


Q. Huang *et al* 2022, *RSC Advances*,12, 32173

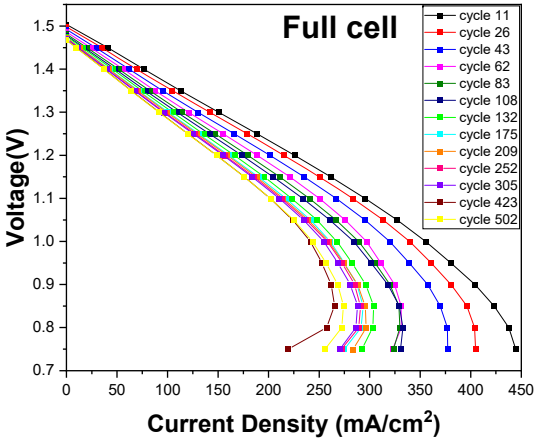
- The cathode showed a much higher overpotential than the anode at both the TOC and BOD over 500 cycles. → the cathode reaction played a more significant role in limiting the capacity.
- The cell performance degradation is more contributed by the anode whose overpotential increased gradually upon long-term cycling whereas the cathode showed the opposite contribution except for the initial 50 cycles.

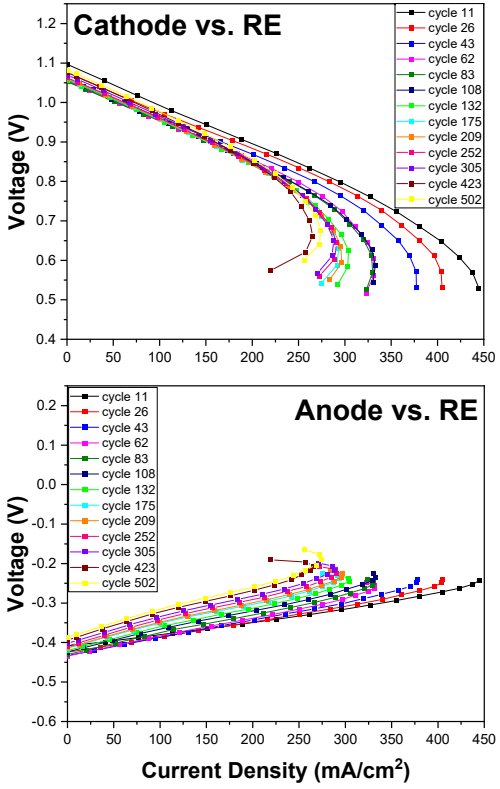
Reliability Investigation by a Stable RE: Polarization Curve

Primary losses: i. kinetic activation polarization; ii. ohmic polarization (iR losses); iii. mass transport



J. Appl. Electrochem., **41**, 1175 (2011)



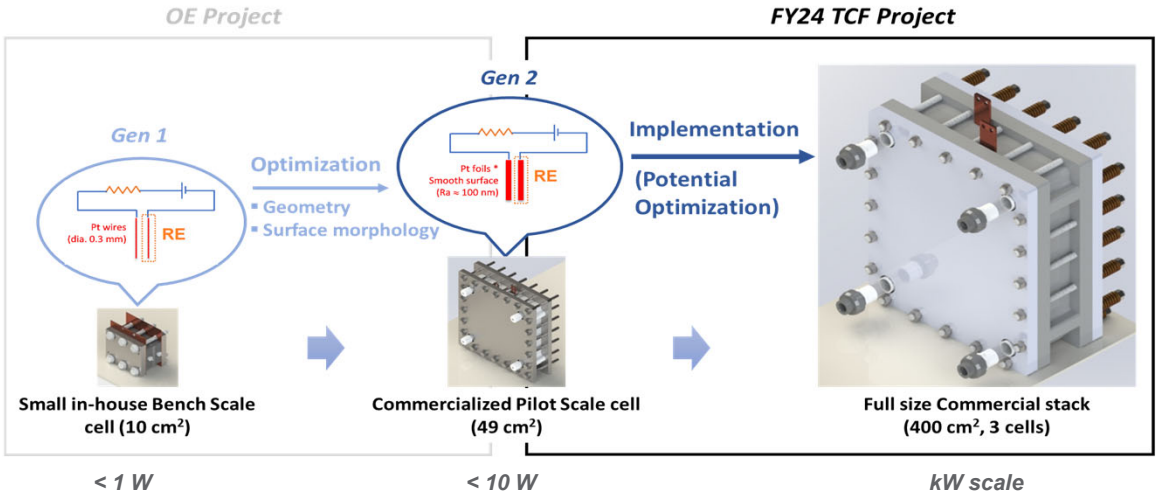


- **Performance loss: increased in the first 100 cycles and then stabilized till 500 cycles.**
- **Ohmic loss: dominated by the cathode, while the anode caused the initial increase.**
- **Transport loss: increased more in the first 100 cycles, contributed by both electrodes.**

Q. Huang *et al* 2022, *RSC Advances*,12, 32173

I. A Stable Reference Electrode Development: Summary

- The newly developed reference electrode, based on a dynamic hydrogen electrode (DHE) with novel design, demonstrated its ultra-long stability over hundreds of cycles, from an in-house to a scaled VRFB.
- By RE approach (to decouple the cathode and anode) combined with voltage profile, overpotential, and polarization curve measurements, the reliability and degradation mechanism of a scaled all-vanadium RFB were investigated, revealing the diverse behaviors of individual electrodes.
- Future work: application development as *in-situ* system diagnostics tool for RFBs – FY24 Technology Commercialization Fund project (OE Funding).



Outline

- A Stable Reference Electrode Development
  - Multi-Gen Development
  - Reliability Investigation by a Stable RE

- **Accelerated Stressor Lifetime Testing (ASLT) Protocols Development**
  - Testing Procedure Development
  - Stressor Study

II. Accelerated Stressor Lifetime Testing (ASLT)

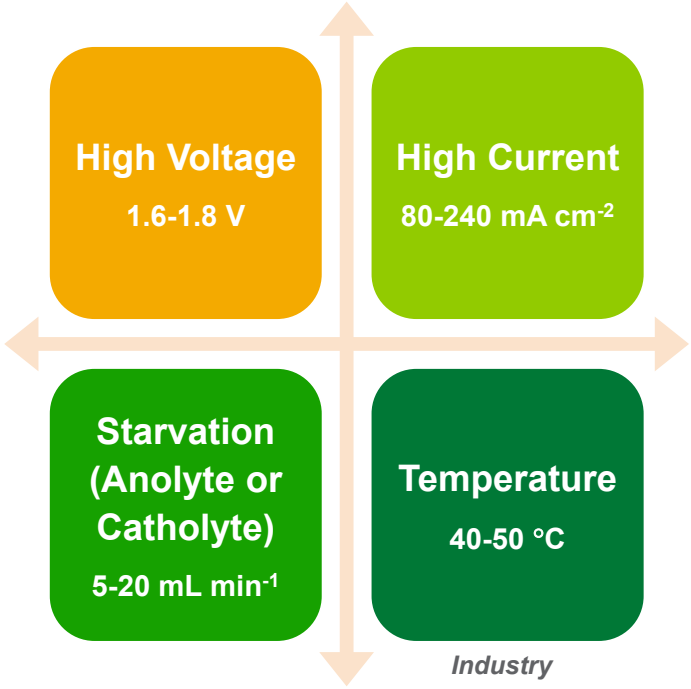
Accelerated Stressor Lifetime Testing

- By selecting appropriate stressors and their levels, VRFB degradation can be accelerated.
- The ASLT results could be correlated with real lifetime.

The testing procedure has been developed for ASLT protocol, with accelerated stressors screened, selected and tested: high voltage, high current, and starvation.

- *"In-situ Reliability Studies of Vanadium Redox Flow Batteries: High Voltage Stressor" 2019 DOE OE Energy Storage Program Peer Review Poster, and 2020 ESS Safety & Reliability Forum Poster.*

- *"In-situ Reliability Investigations of Vanadium Redox Flow Batteries: An Ultra-Stable Reference Electrode Development & High Current Stressor Study" 2021 DOE OE Energy Storage Program Peer Review Poster.*



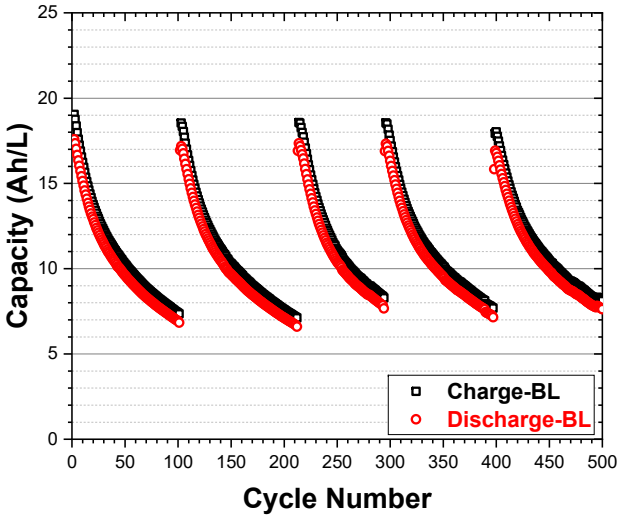
Stressor screening and selecting by literature study and preliminary experiments

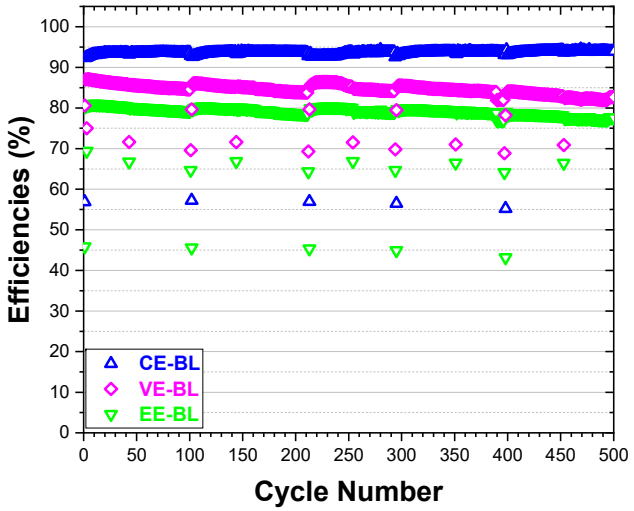
ASLT Protocols Development: Baseline Testing Procedure

Commercial cell: 49 cm^2 *Commercial electrolyte: 1.6 M V, ~2 M H_2SO_4* *Membrane: Nafion®*

At every 50 cycles:
- EIS & polarization curve measurement at the top of charge; sampling at the bottom of discharge

At every 100 cycles:
- Electrolyte remixing





- **Voltage: 0.8-1.6 V**
- **Current density: 80 mA cm^{-2}**
- **Flow rate: 80 mL min^{-1}**
- **Temperature: @ 25 °C (RT)**

Performances	Baseline (BL)
Initial Charge Capacity (Ah/L)	30.7
Initial Discharge Capacity (Ah/L)	17.4
CE (%)	93-94
VE (%)	84-87
EE (%)	79-81

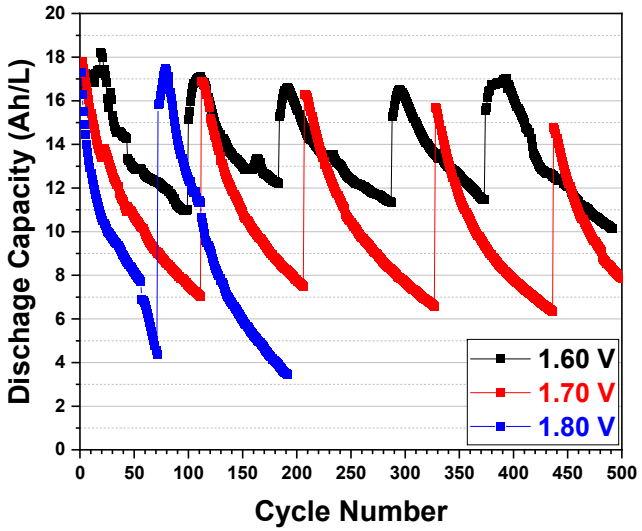
The capacity can be completed recovered by the remixing, but the efficiencies (VE) can not, indicating the degradation of the cell (electrode) during long-term cycling.

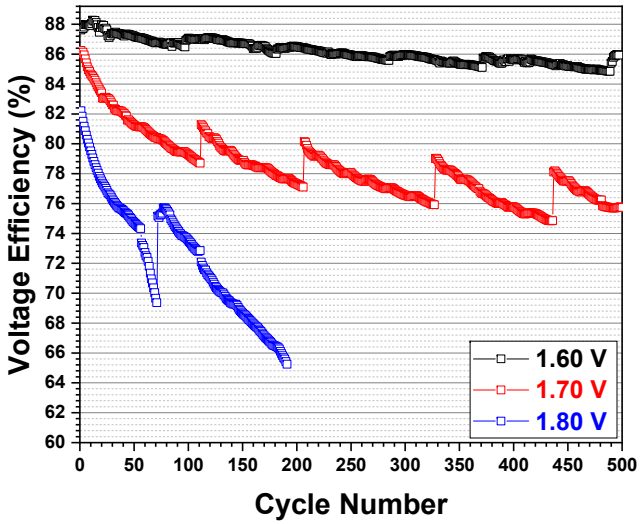
Stressor Study: High Voltage

Upper Voltage Limit: 1.6 V - 1.8 V

- Voltage: 0.8-1.6 V
- Current density: 80 mA cm^{-2}
- Flow rate: 80 mL min^{-1}
- Temperature: @ 25 °C (RT)

Cell Performance: Capacities & Efficiencies





Potential side reactions:
- Anode: HER
- Cathode: Oxidation of electrode ($C \rightarrow CO_2$)

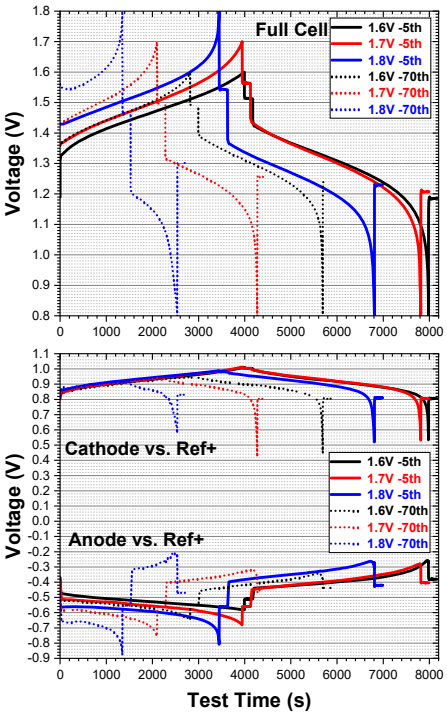
Electrolyte imbalance
Electrode degradation

- **Increasing upper voltage causes more significant decay in cell performance: capacity and VE.**
- **By electrolyte remixing, the capacities can be recovered mostly, but the VE can only be recovered partially (by 50 % or less), indicating a higher upper voltage causes electrode (surface) degradation.**

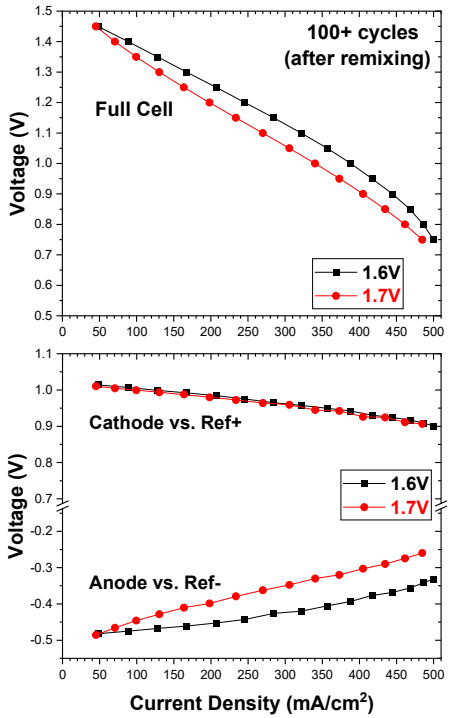
Bin Li & Rajankumar Patel
(Manuscript in preparation)

Stressor Study: High Voltage (Cont.)

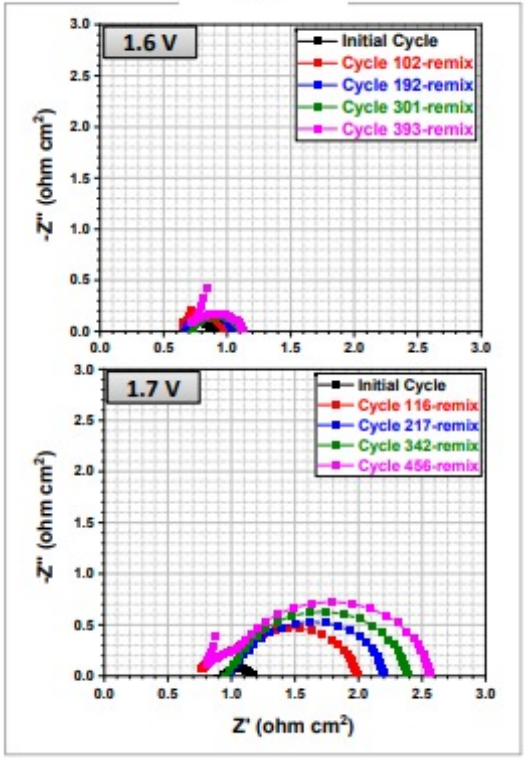
Voltage Profile



Polarization Curves



EIS



- Increasing upper voltage causes more significant performance decay due to the increase in polarization and charge transfer resistance and affects more on the anode and membrane than the cathode.
- Electrolyte remixing can recover the capacity fading (crossover), but it can not recover the resistance increase (electrode degradation).

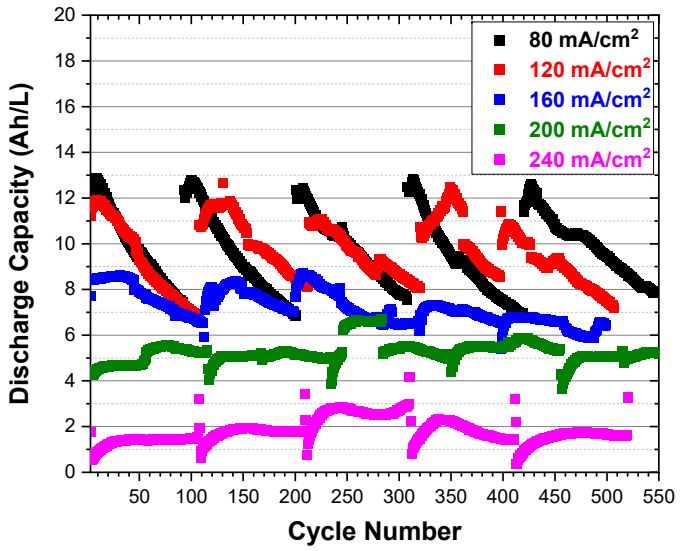
Bin Li & Rajankumar Patel (Manuscript in preparation)

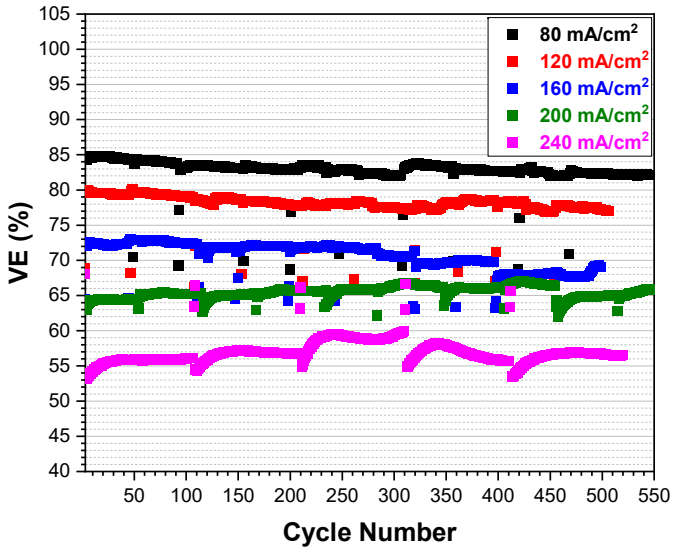
Stressor Study: High Current

High Current: 80 - 240 mA cm^{-2}

- Voltage: 0.8-1.6 V
- Current density: 80 mA cm^{-2}
- Flow rate: 80 mL min^{-1}
- Temperature: @ 25 °C (RT)

Cell Performance: Capacities & Efficiencies





Increasing current density

↓

Overall cycle time reduction

↓

Diffusion suppression (Nafion®)

↓

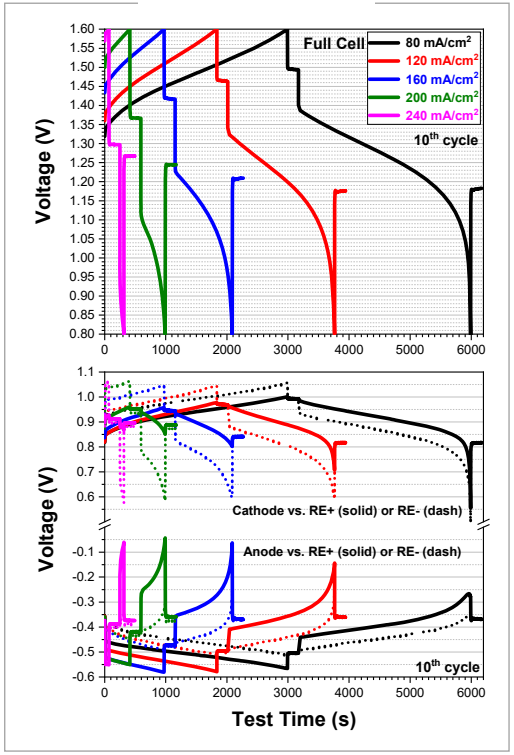
Net convective crossover reduction

Increasing current density causes a significant decrease in cell performance (capacity & VE), but a less significant performance decay during cycling (@ 160 mA/cm² or more).

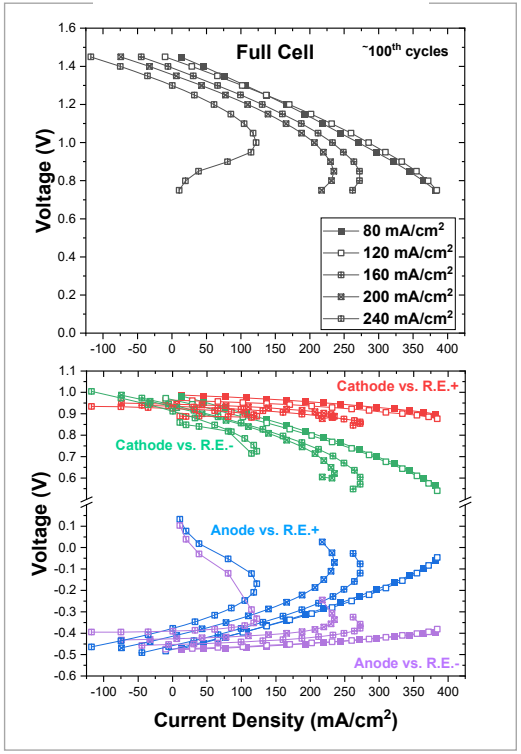
Manuscript in preparation

Stressor Study: High Current (Cont.)

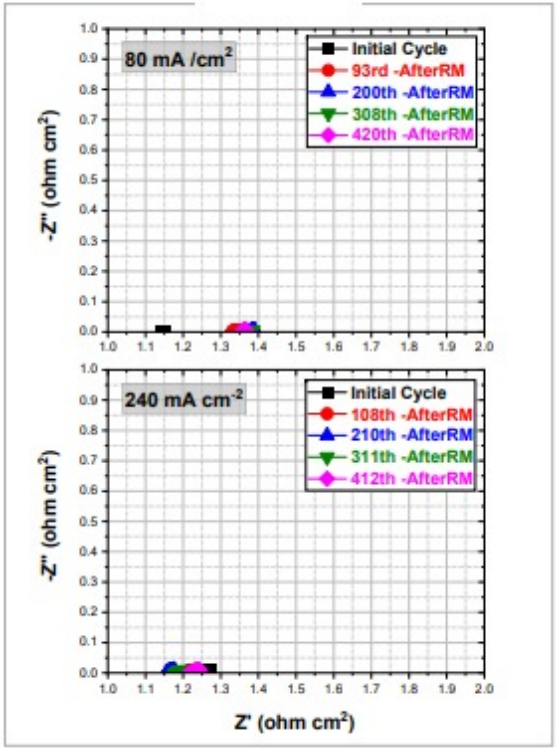
Voltage Profile



Polarization Curves



EIS



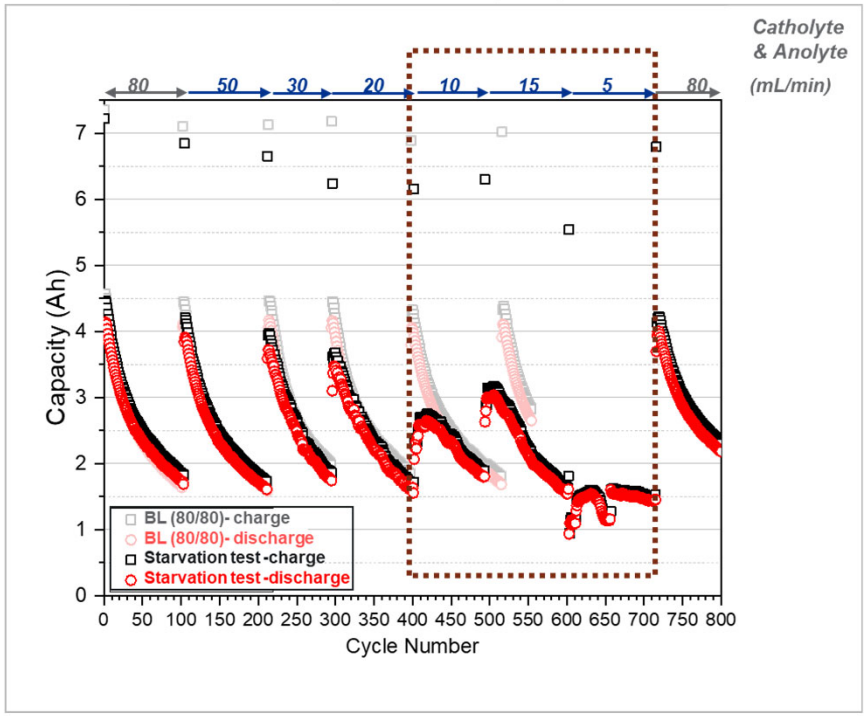
Manuscript in preparation

Increasing current density causes:

- **Significant increase in overpotential (mass transport loss) – more dominated by the membrane and anode.**
- **Insignificant increase in resistance (ohmic or charge transfer) – indicating neglectable electrode degradation.**

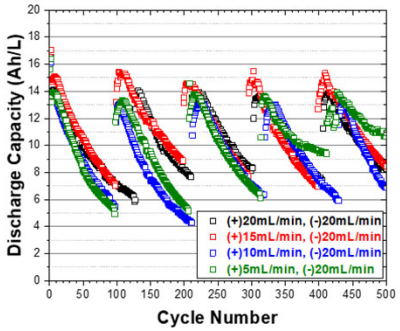
Stressor Study: Starvation

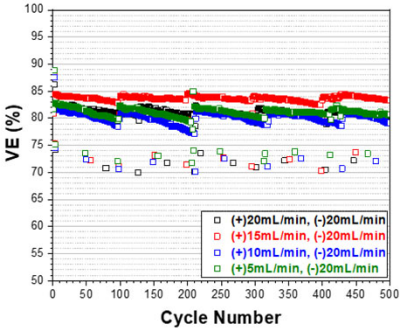
Starvation (Flow Rate) Exploration



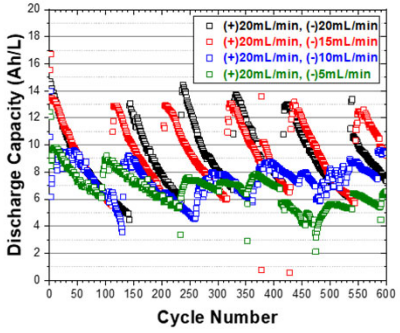
The starvation of catholyte or anolyte is defined as in the range of 5-15 mL/min of flow rate.

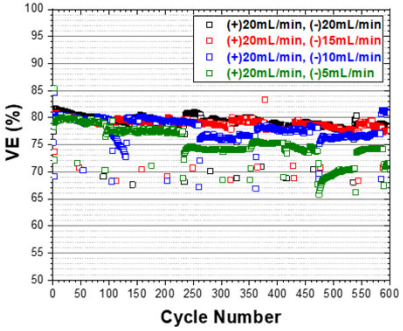
(+) Catholyte Starvation: 15, 10, 5 mL/min





(-) Anolyte Starvation: 15, 10, 5 mL/min



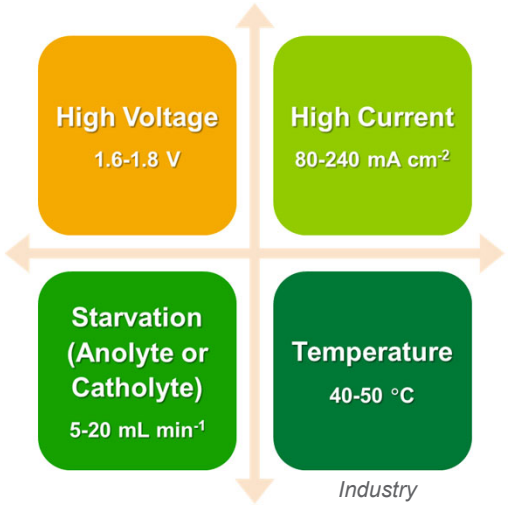


Anolyte starvation affects cell performance more than catholyte starvation: slower kinetics for anode reaction (V^{2+}/V^{3+}) than cathode reaction (VO^{2+}/VO_2^{+}).

Manuscript in preparation

II. ASLT Protocols Development: Summary

- The testing procedure has been developed for ASLT protocol, with accelerated stressors screened, selected and tested: high voltage, high current, and starvation.
- All selected stressors accelerated the cell degradation, in which high voltage affected the electrode degradation that is irreversible while high current and starvation mostly affected the imbalance of electrolyte that is reversible (by electrolyte remixing).
- Future work:
  - Mechanism study by further characterizations and data analysis.
  - Modeling to establish the ASLT protocol and predict the lifetime of VRFB.



Acknowledgements

- We acknowledge the support of Dr. Imre Gyuk and the OE Energy Storage Program for this work.

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Thank you

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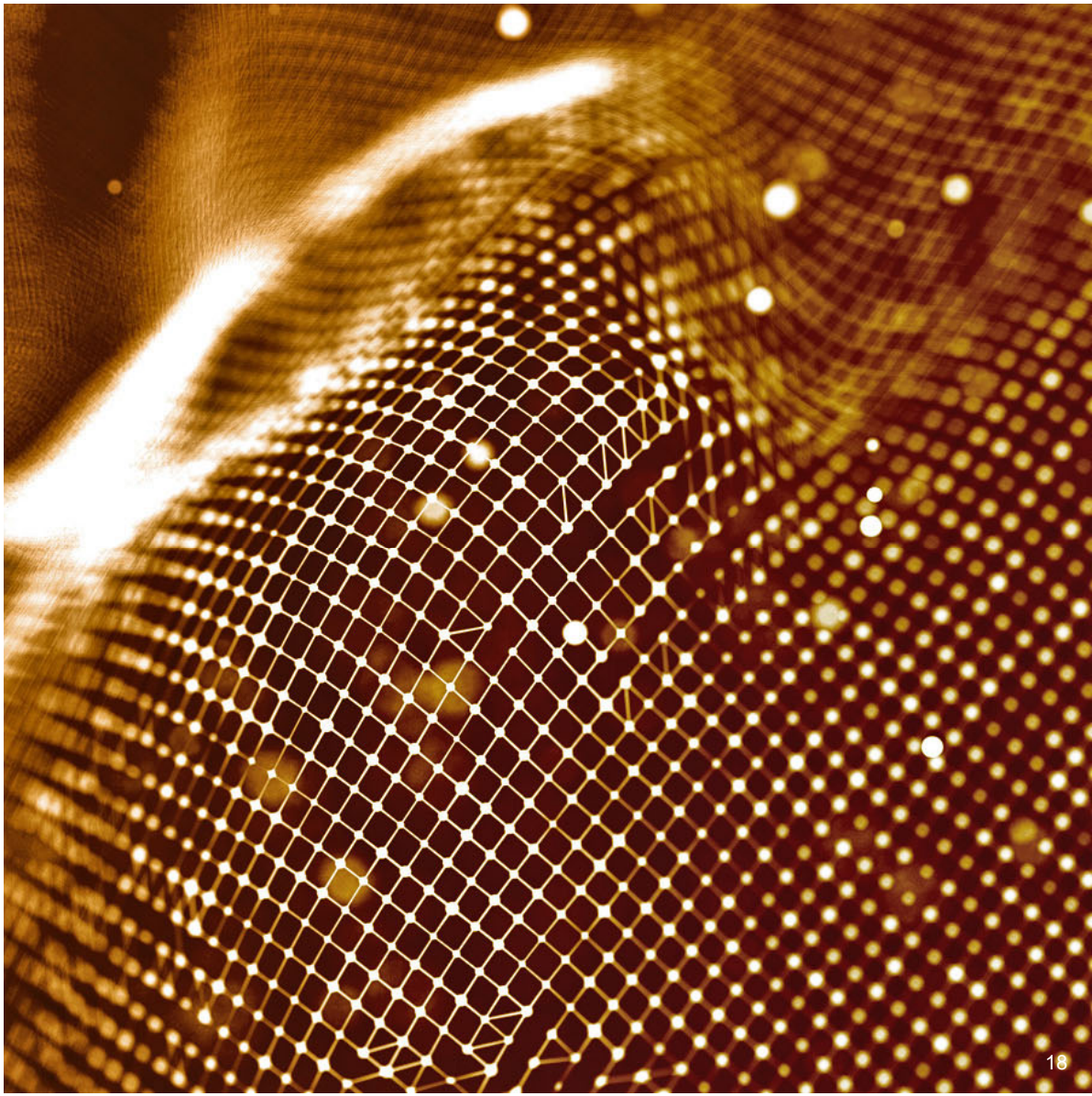

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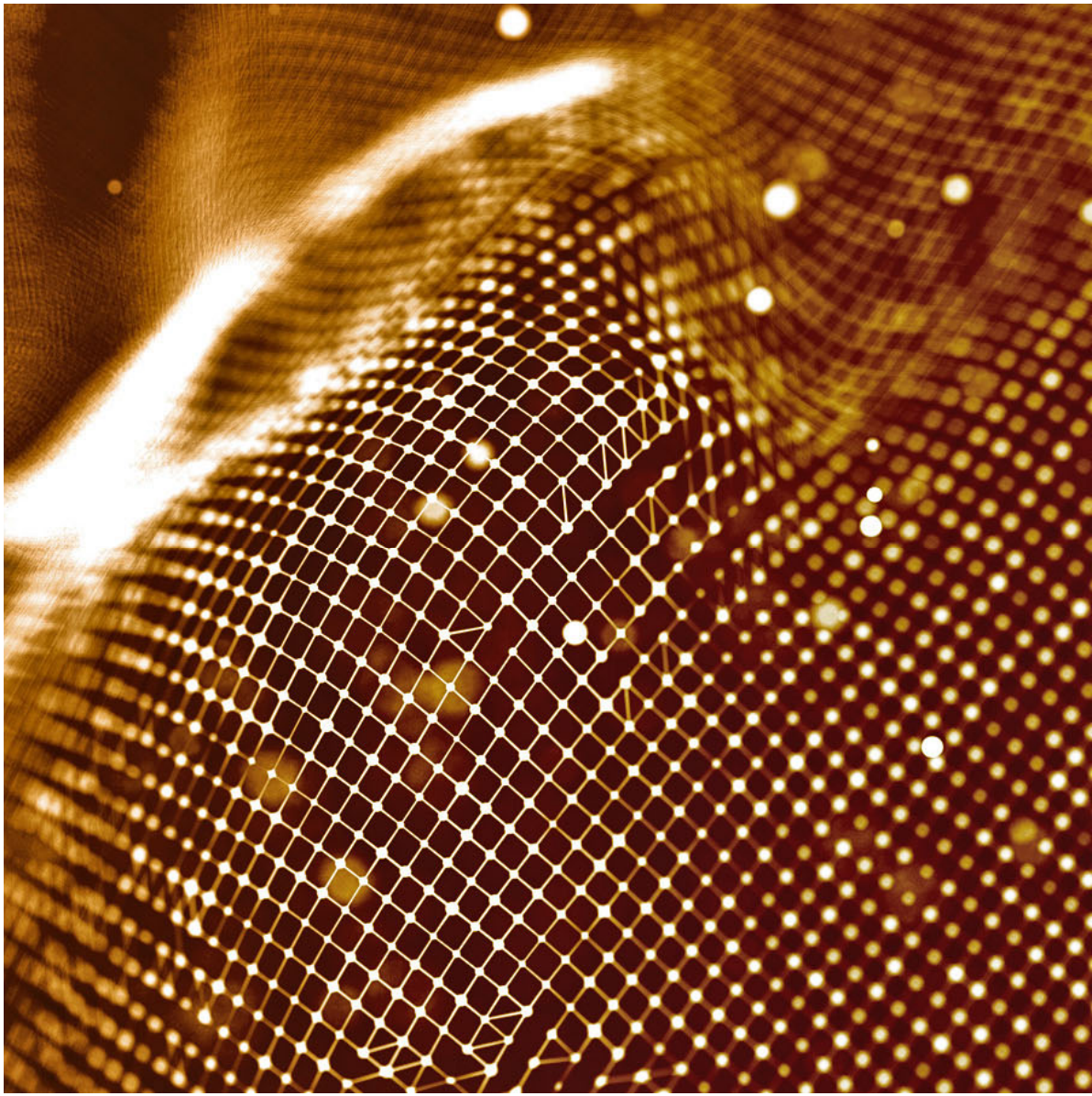
Backup



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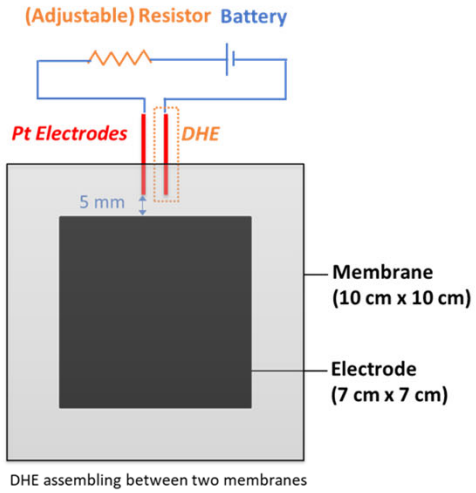
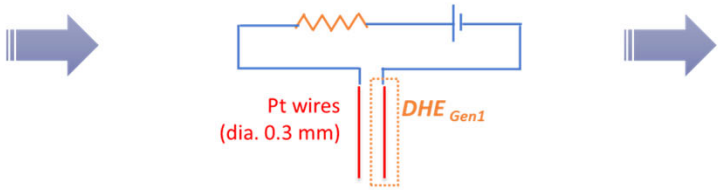
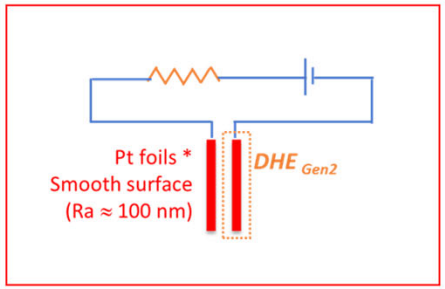
A Stable Reference Electrode Development:

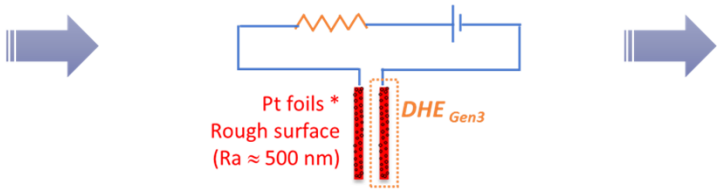
from an In-House Cell to a Scaled Cell



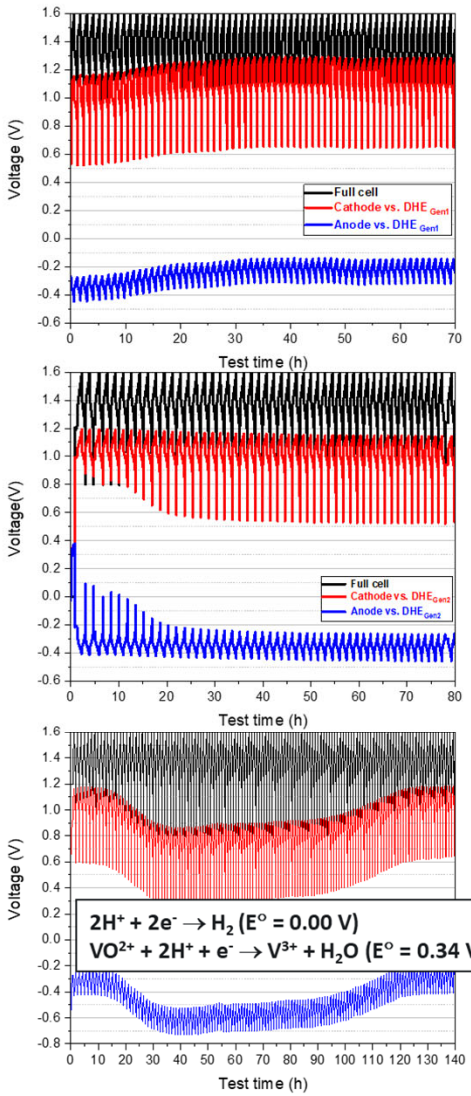
DHE assembling between two membranes





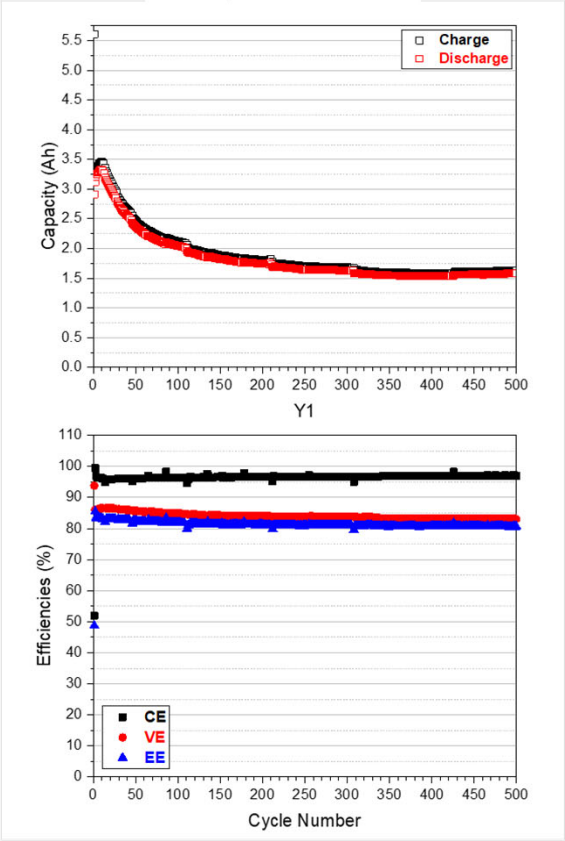


The high stability of DHE in a scaled cell can be achieved by optimization of the DHE design (the area and surface roughness of Pt electrodes)

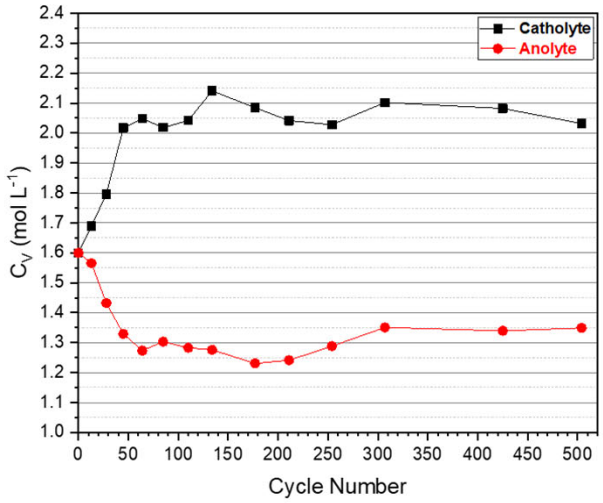


Reliability Investigation on a Scaled VRFB

Cell performance



Negative-to-positive transfer of vanadium ions



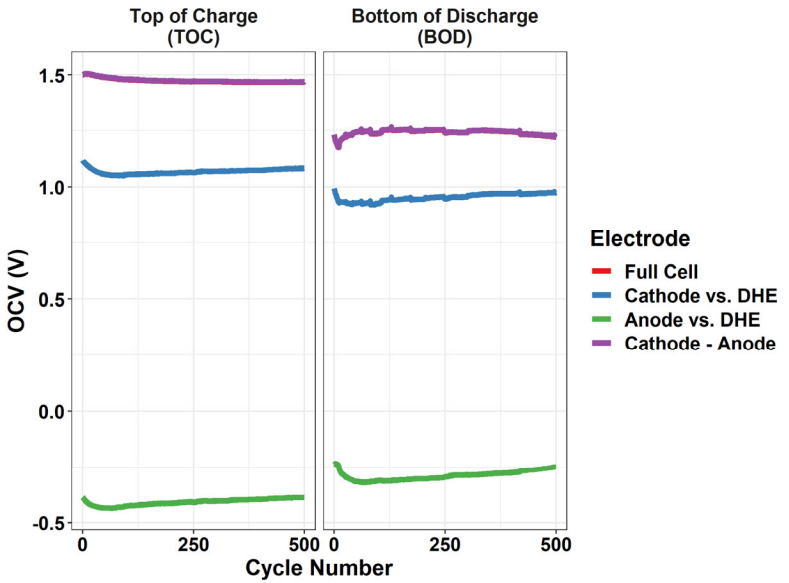
The most significant capacity fading related performance degradation happened in the initial 100 cycles, which is associated with the imbalanced vanadium active species between catholyte and anolyte induced by electrolyte crossover.

Voltage Profile → **Overpotential** → **Polarization Curve**

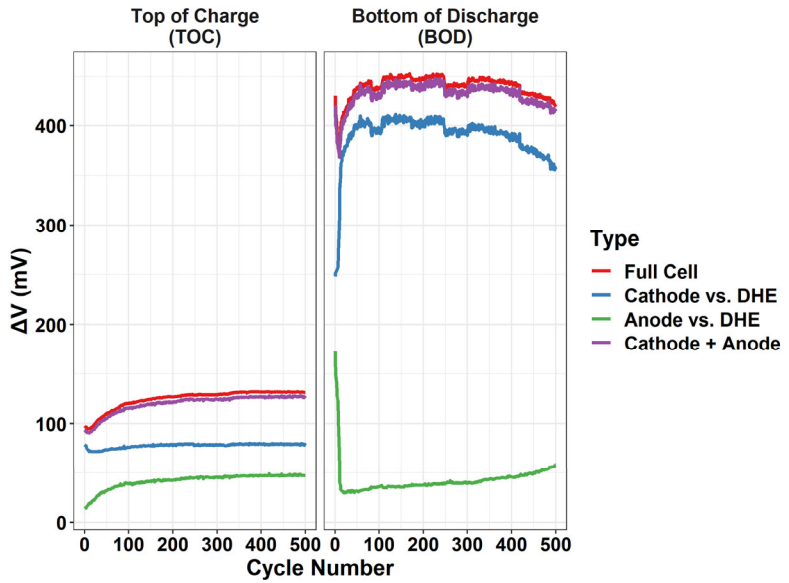
Electrolyte: 1.6 M vanadium; Membrane: N212 x2

Reliability Investigation on a Scaled VRFB: Overpotential

OCV



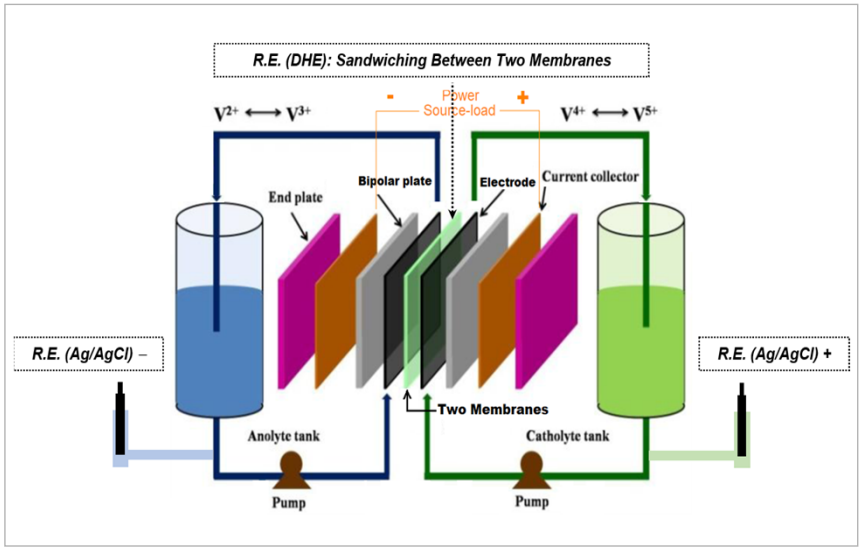
Overpotential (ΔV)

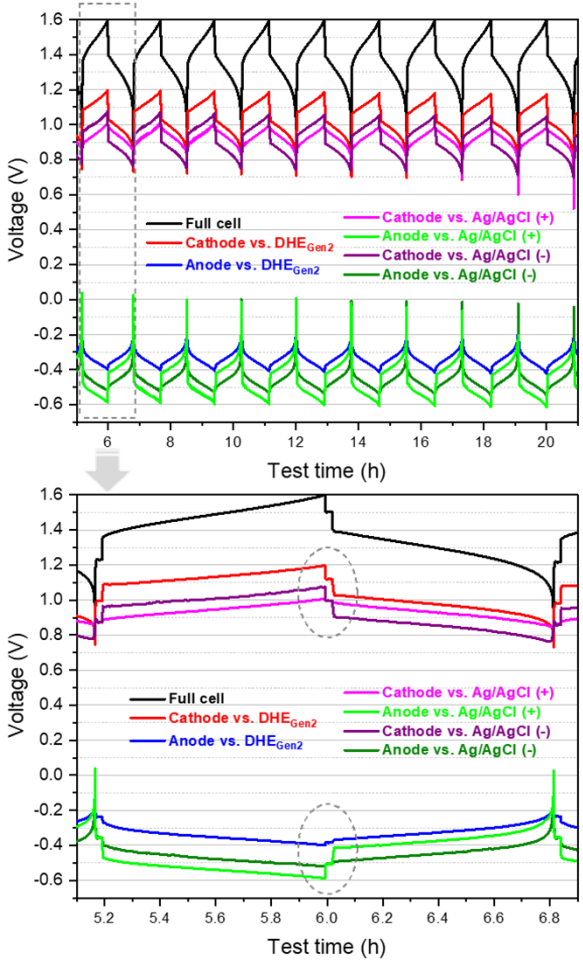


- The cathode showed a much higher overpotential than the anode at both the TOC and BOD throughout 500 cycles
  → the cathode reaction played a more significant role than the anode reaction in limiting the capacity.
- The cell performance degradation is more contributed by the anode whose overpotential increased gradually upon long-term cycling whereas the cathode showed the opposite contribution except for the initial 50 cycles.

Reliability Investigation on a Scaled VRFB

In-situ Setup: Internal DHE & External Ag/AgCl REs





- The consistent pattern of cathode or anode voltage curves (vs. different REs) demonstrate the high stability of the newly developed DHE.
- The gaps among three voltage curves of each individual electrode includes the differences in (a) the potential of REs and (b) the overpotential from membrane effects.