Naval Postgraduate School
Energy Academic Group
Defense Energy Seminar Series
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Dual-Layer Energy Storage:

Combining Redox Flow Batteries *With Renewable Hydrogen Generation*

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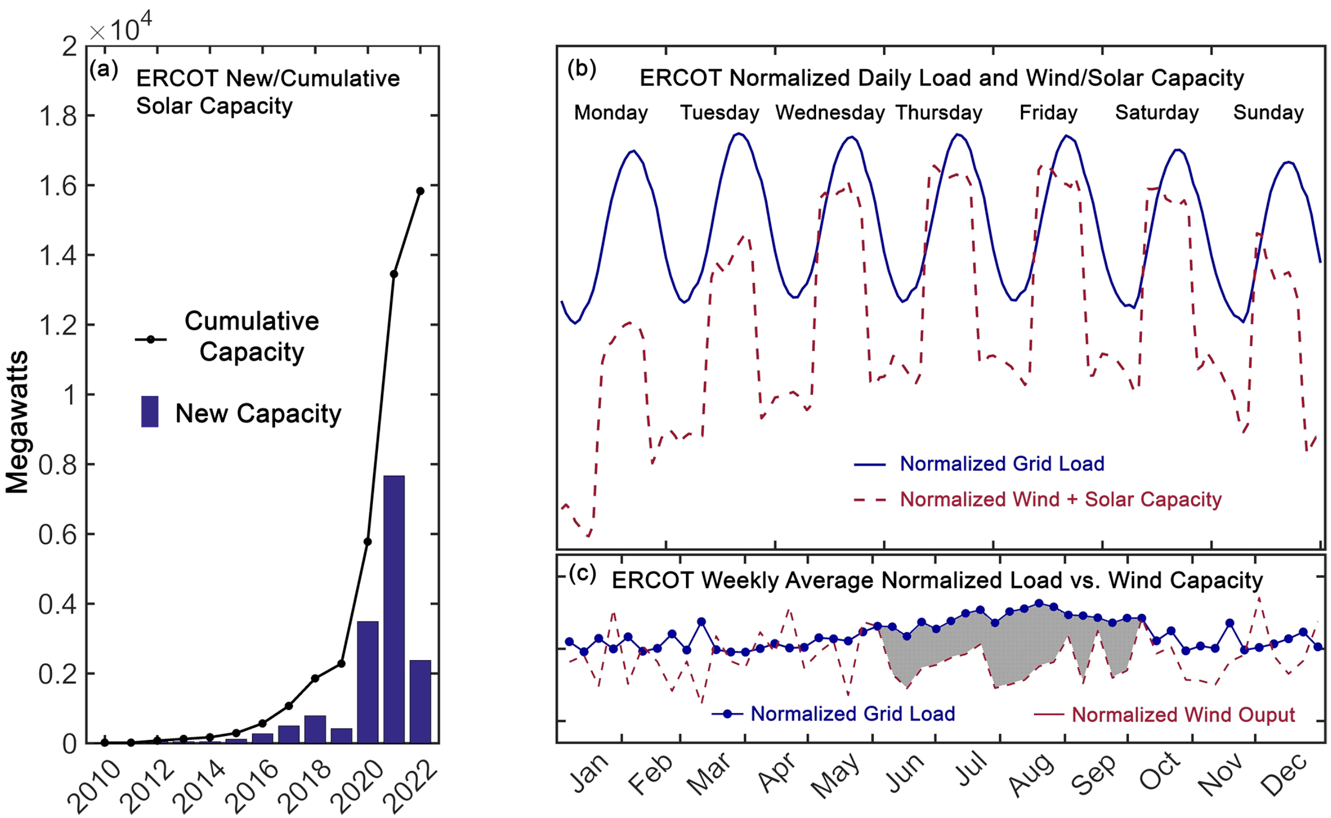
ELECTROCHEMICAL ENERGY SYSTEMS AND TRANSPORT LABORATORY

The Need: Grid-Scale Energy Storage



Bad News

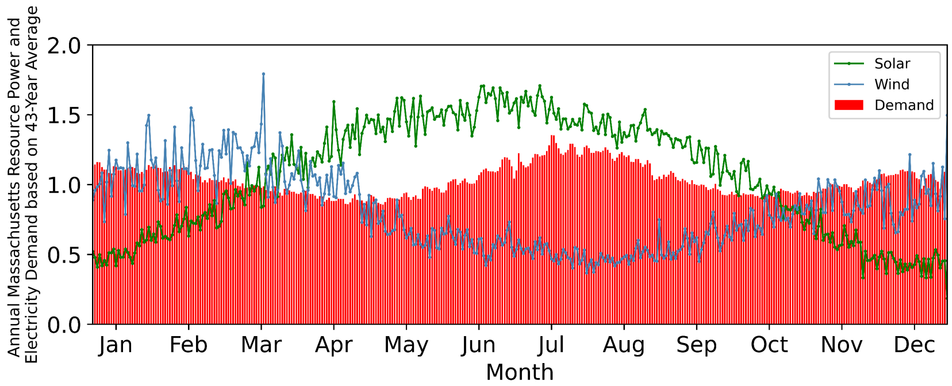
Intermittency on short time-scales

Intermittency on long time-scales

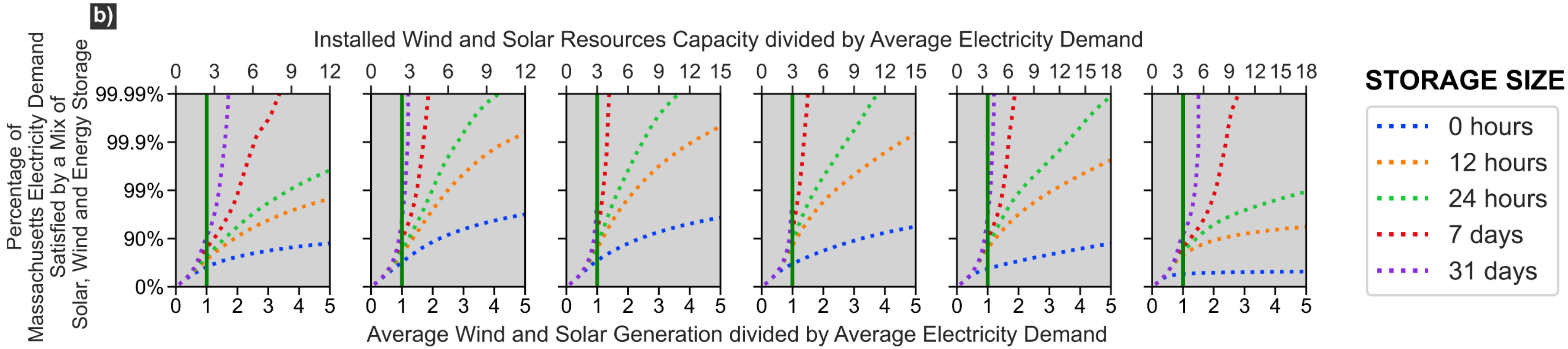
Grid-scale *long-duration energy storage* has become a **"need to have" vs a "nice to have"** to enable a renewable grid.

Pahari, S., et al., *RSC Advances,* **2021**, 11 (10), 5432-5443

The Need: Long-Duration Energy Storage



- 43 years of hourly weather data from NASA MERRA-2
- Massachusetts' electric supply and demand is investigated

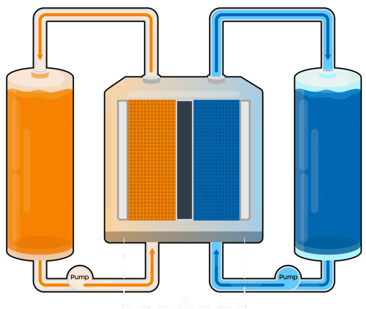


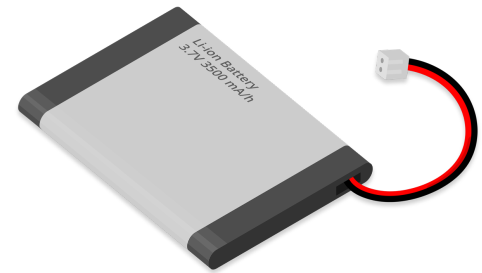
Grid-scale ***long-duration energy storage*** is the key for resiliency without excessive over-generation

Freeman, S., Agar, E. *Under Review*, **2023**

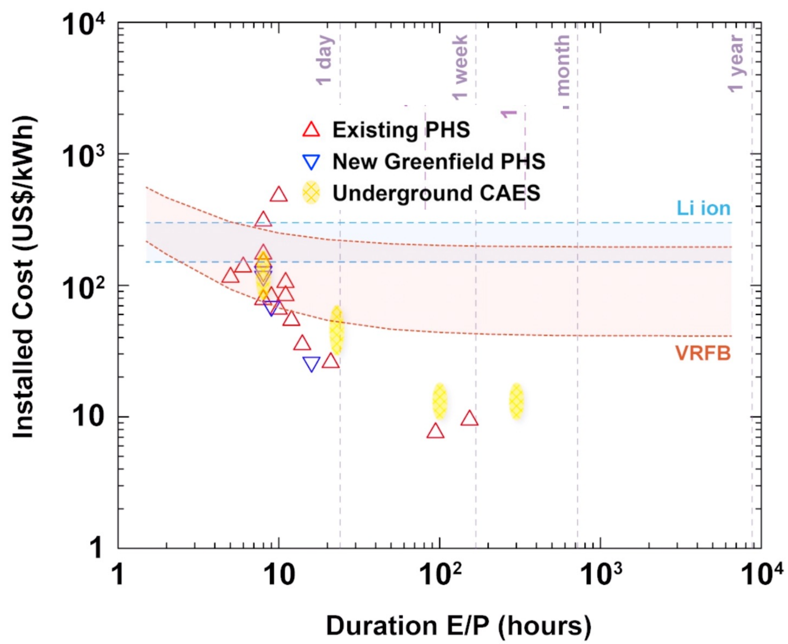
The Solution: Redox Flow Batteries

The Solution: Redox Flow Batteries





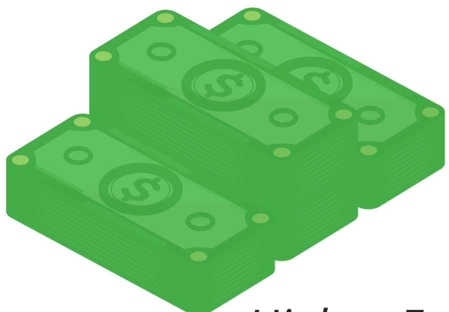
Decoupled power outpu storage - scalability	nd energy storage
Economic energy storag	gy storage h
No capacity fade (VRFB) lifetime	ss in 10 years
Safety: Stable Non-flam (Aqueous)	ard
Active material can be e valuable end-of-life pro	clable (for now)



F. R. Brushett and Y-M Chiang et al., *Joule*. **2017**, 1, 306-327.

The Solution: Redox Flow Batteries

Cost is a major challenge **(Dept. of Energy Target <$100 /kWh)**



Performance →

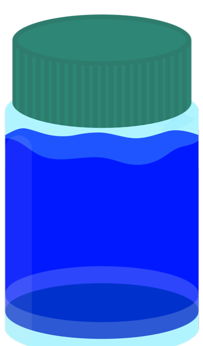
Higher Energy Density

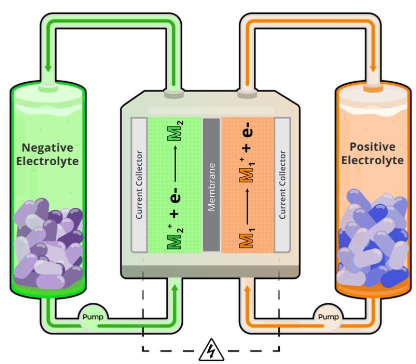
Higher Power Density

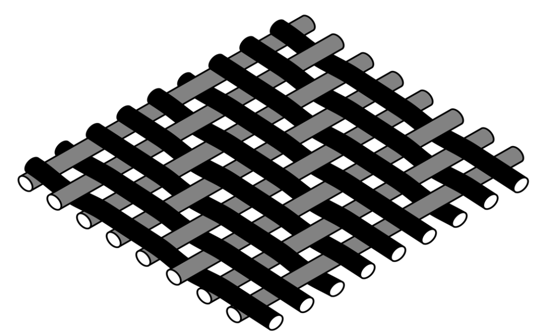
Thrust 1

Thrust 2

Thrust 3





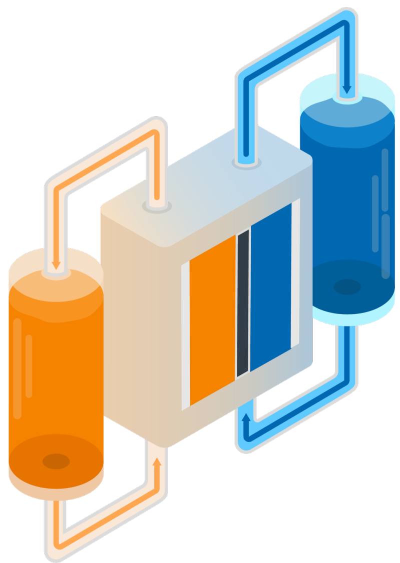


Electrolyte: Cell Potential

Electrolyte: Solubility Limitation

Electrode: Tailored design for RFBs

he Problem: Intrinsic Solubility Limitation



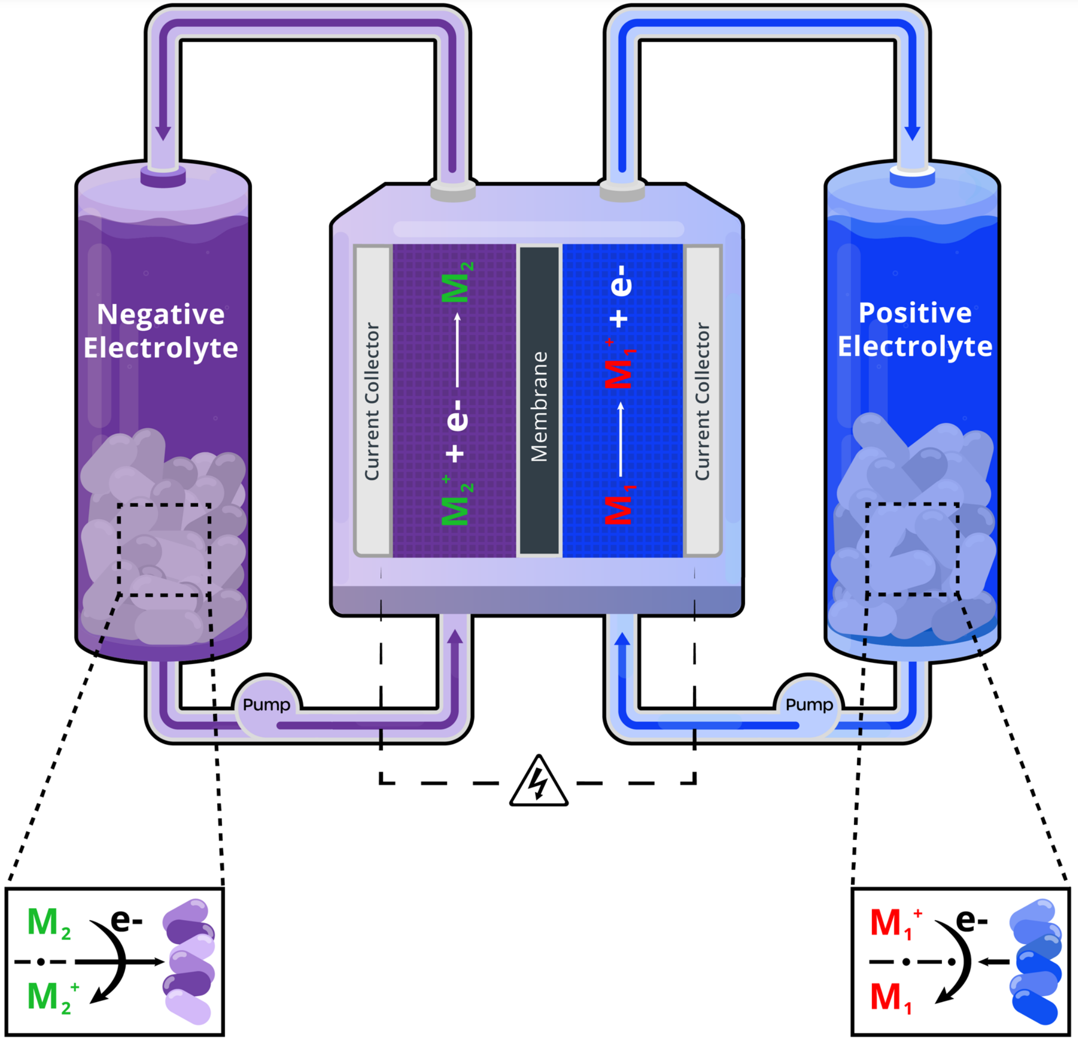
Redox flow batteries[1]	< 100 Wh·L^{-1}
Li-ion battery[2]	< 750 Wh·L^{-1}
Hydrogen (liq)	2,300 Wh·L^{-1}

Energy density → *n: number of transferred electrons*; *E: the flow battery cell voltage*; *C: active species concentration*

- Energy density is **intrinsically limited** by the **solubility**
- Difficult to yield disruptive improvements in energy density

[1] X. Wei et al., *ACS Energy Letters*, **2017**, 2, 2187-2204
[2] K. Gong, Q. Fang, S. Gu, S. Li, Y. Yan, *Energy & Environmental Science*, **2015**, 8, 3515–3530.

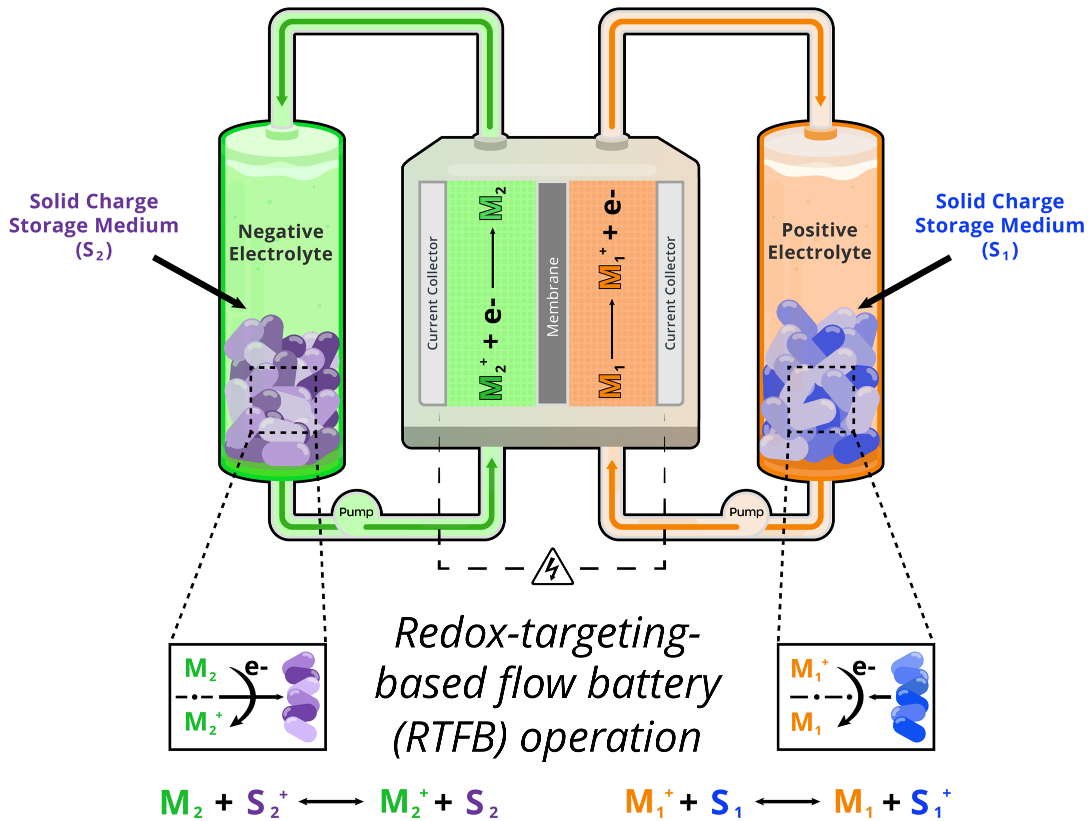
Project 1: Overcoming the Active Material Solubility Limitation via Indirect Redox Targeting Reactions



$M_2 + S_2^+ \longleftrightarrow M_2^+ + S_2$ $M_1^+ + S_1 \longleftrightarrow M_1 + S_1^+$

N00014-20-1-2858

roject 1: Indirect Redox Targeting Reaction



At electrode in flow cell

$$M_1 \longleftrightarrow M_1^+ + e^-$$

$$M_2^+ + e^- \longleftrightarrow M_2$$

In external tanks

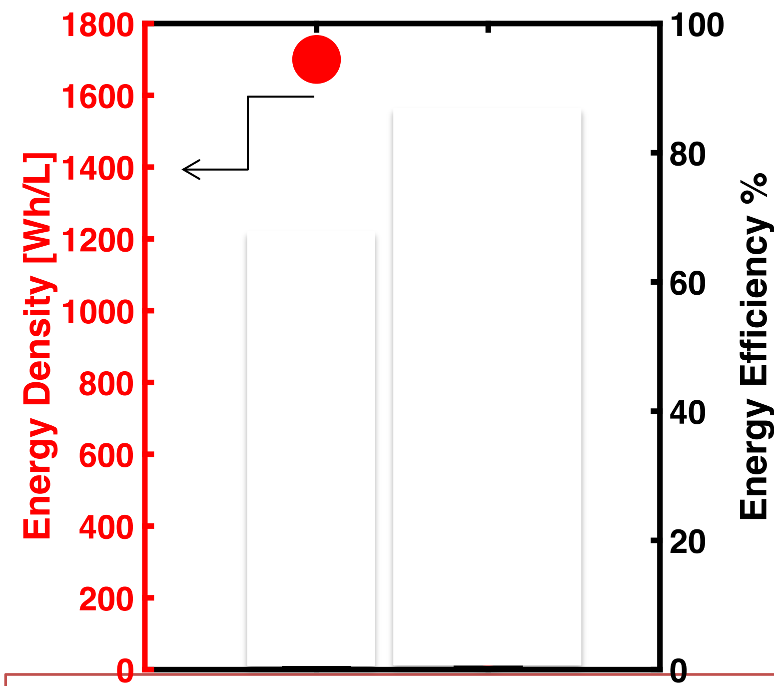
$$M_1^+ + S_1 \longleftrightarrow M_1 + S_1^+$$

$$M_2 + S_2^+ \longleftrightarrow M_2^+ + S_2$$

Redox mediator (M) shuttles charge between the flow cell and the solid charge storage medium (S) in the tanks – **combining high energy density of Li-ion and scalability of RFBs**

M. Zhou et al., *Chem*, **2017**, 3, 1036-1049.
R. Yan, Q. Wang, *Advanced Materials*, **2018**, 30, 1802406.
X. Wang et al., *Current Opinion in Electrochemistry*, **2021**, 29, 100743.

roject 2: Redox Mediated Water Electrolysis



All Vanadium Redox Flow Battery → **PEM or AEM Electrolyzer**

Grid Scale Energy Storage

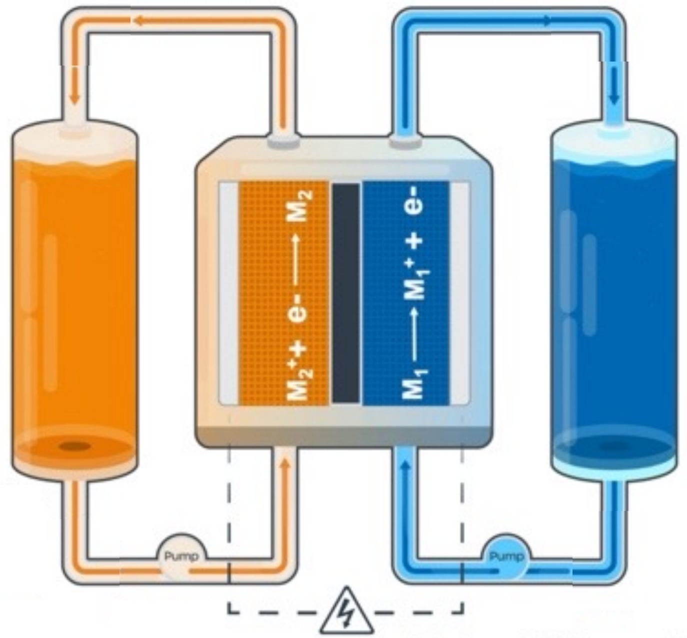
Aviation, Road Transport, Manufacturing

- Technology hybridization enables **maximum utilization of renewable energy**
- **Overcome low energy density** of conventional all vanadium RFBs
- Indirect water electrolysis will **mitigate gas cross over issues**

IRENA, Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.50C Climate Goal, 2020
IEA, Share of low-carbon sources and coal in world electricity generation, 1971-2021

roject 2: Redox Mediated Water Electrolysis

Two in One Approach



Electrochemical
Energy Storage

In Redox Mediators

Typical RFB Operation

Dennison, Chimia, 2015, 69, no. 12
Xianfeng Li, Joule 3, (2019), 2066-2067
Reynard and Girault, Cell Reports Physical Science (2021)

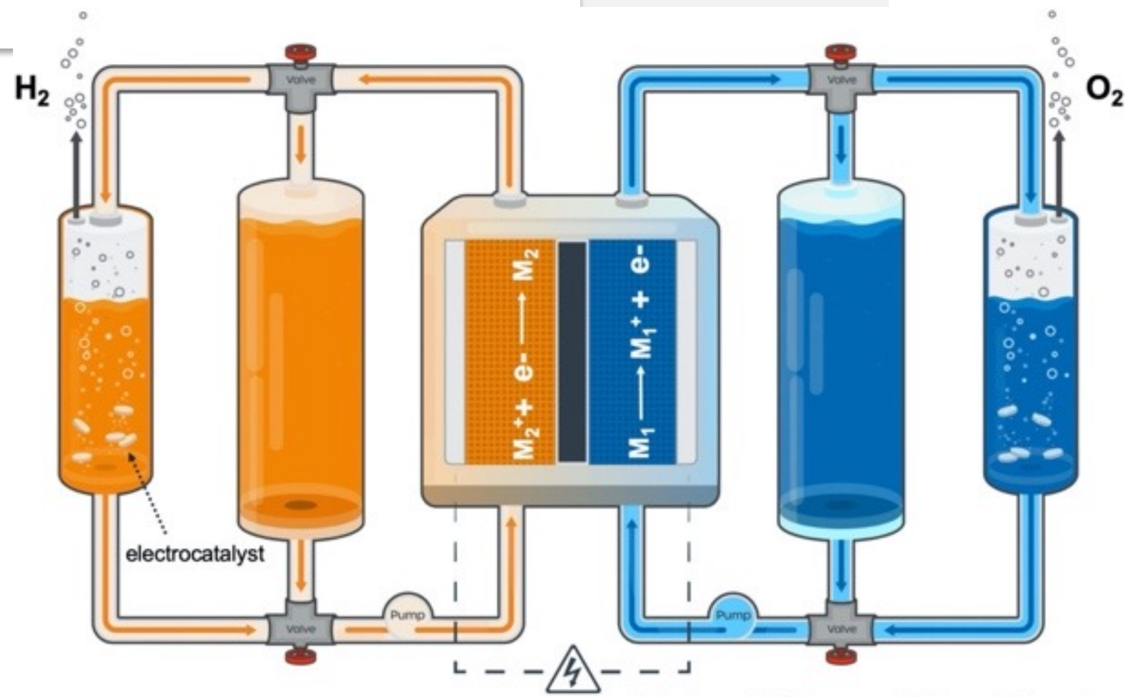
Project 2: Redox Mediated Water Electrolysis

Two in One Approach

Chemical Energy Storage

Hydrogen Fuel

Indirect Water Splitting



Electrochemical Energy Storage

In Redox Mediators

Typical RFB Operation

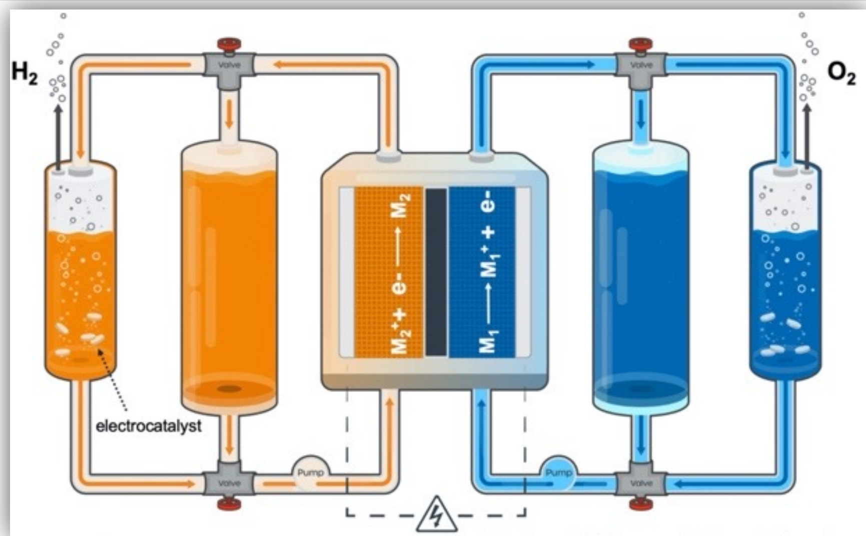
$$2H^+ + 2M_2 \rightarrow 2M_2^+ + H_2$$

$$2H_2O + 2M_1^+ \rightarrow 2M_1 + 4H^+ + O_2$$

Charged redox mediator (RM) is discharged chemically in separate external reactors containing electrocatalyst – **redox mediated water splitting**

Dennison, Chimia, 2015, 69, no. 12
Xianfeng Li, Joule 3, (2019), 2066-2067
Reynard and Girault, Cell Reports Physical Science (2021)

Key Role : Redox Mediators



$2H^{++2V_2^{+\rightarrow 2V_3^{++2H_2}}}$

ALL VANADIUM

$2H_2O + 2V^{5+\rightarrow 2V^{4++4H^{++O_2}}}$

(vs SHE) = **0.99 V**

Aqueous redox mediator in catholyte should have **thermodynamic potential above 1.23 V** to drive water oxidation

Dennison, Chimia, 2015, 69, no. 12
Xianfeng Li, Joule 3, (2019), 2066-2067
Reynard and Girault, Cell Reports Physical Science (2021)

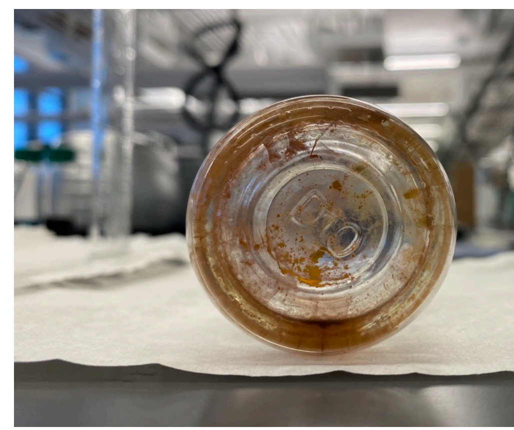
Manganese as Redox Mediators

Possible Transition Metal RMs	Redox Potential vs SHE
Co^{3+}/Co^{2+}	**1.81**
Pb^{4+}/Pb^{2+}	**1.67**
Ce^{4+}/Ce^{3+}	**1.61**
Br^{+}/Br_2	**1.60**
Mn^{3+}/Mn^{2+}	**1.51**
Cr^{6+}/Cr^{3+}	**1.33**
V^{5+}/V^{4+}	**0.99**

Charging

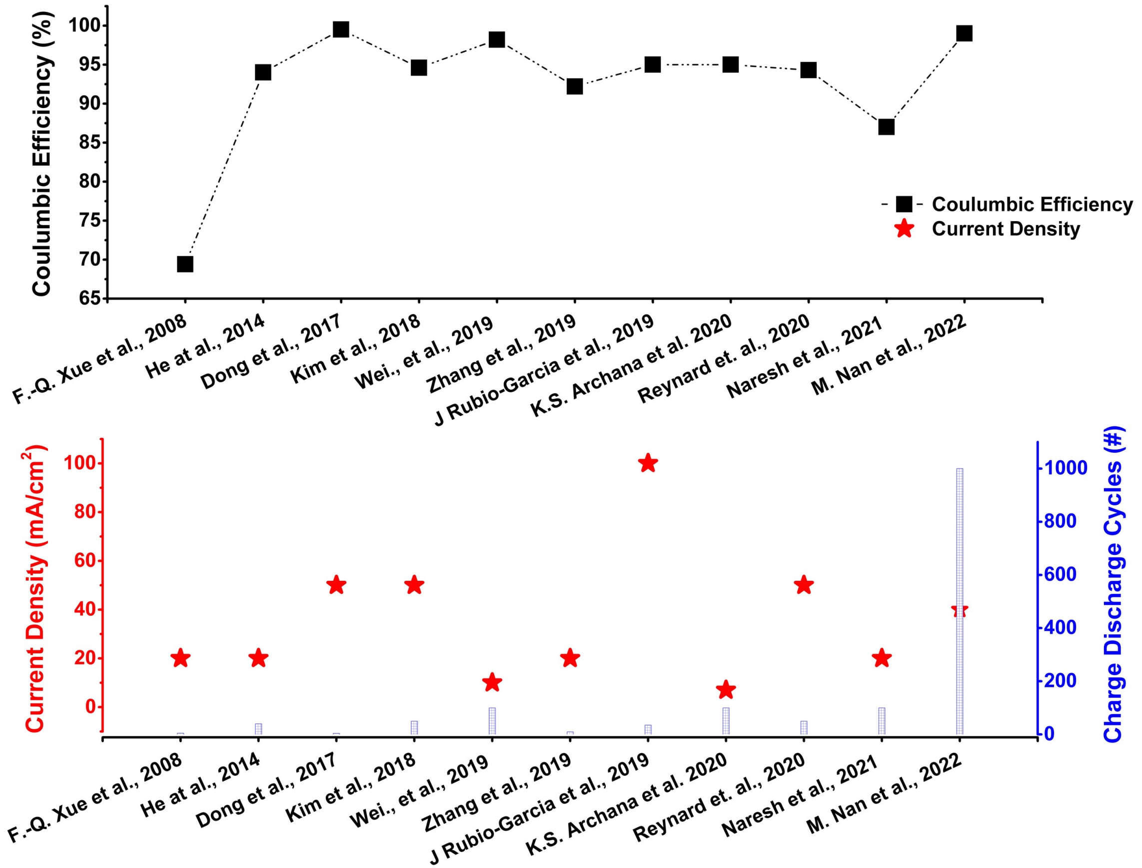
Side Reaction

Rapid Mn^{3+} **disproportionation reaction** leads to solid **MnO_2** precipitate



K., P. W. Atkins: Physical Chemistry, 1990, 94 (10), p. 1171-1171
Pang, S. C., et al., J. Electrochemical Society, 2000, 147 (2), 444
F.-Q. Xue et al., Electrochimica Acta 53, 2008, 6636–6642

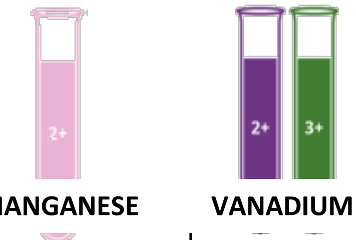
Ianganese-based Redox Flow Battery



Current state of art performance for Manganese RFBs. ***The coulombic efficiency of RFB drops due to MnO_2 precipitation limiting the state of charge***

roblem Statement : State of Charge Trade-off

Stability of Redox Mediator | Electrochemical Performance | Hydrogen Generation



1

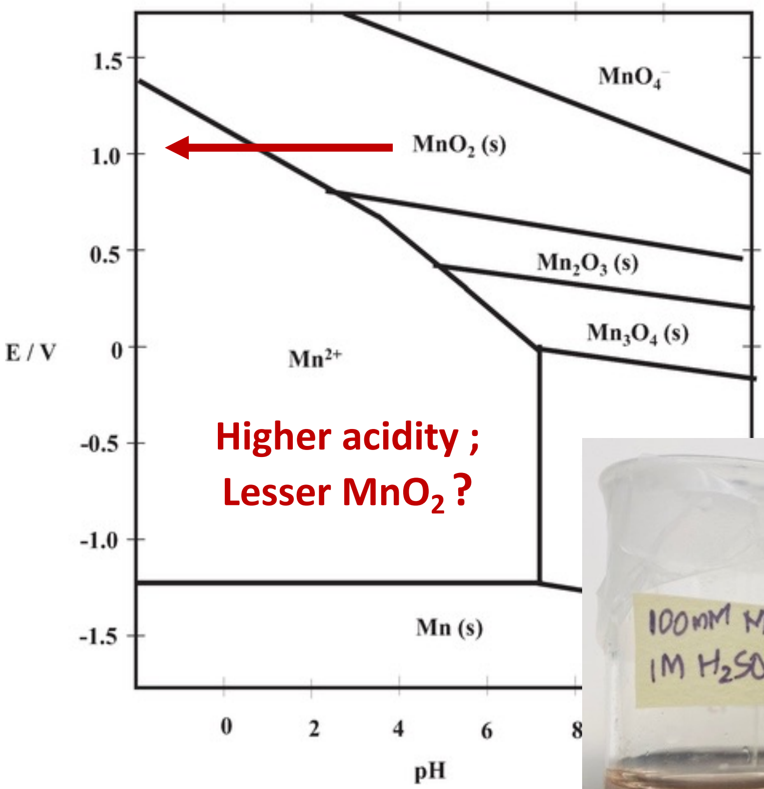
2

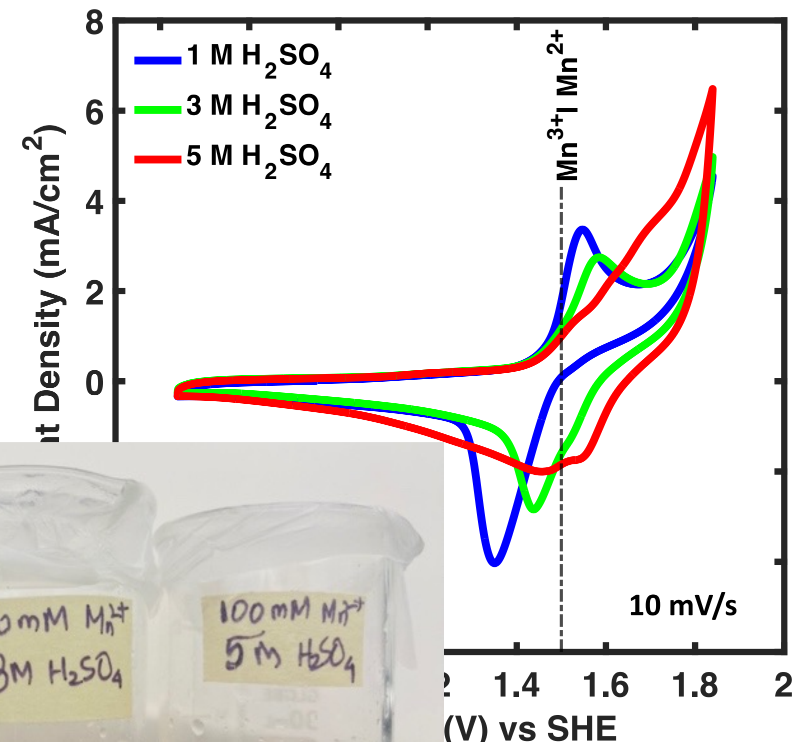
MnO_2 aggravates at higher SOC

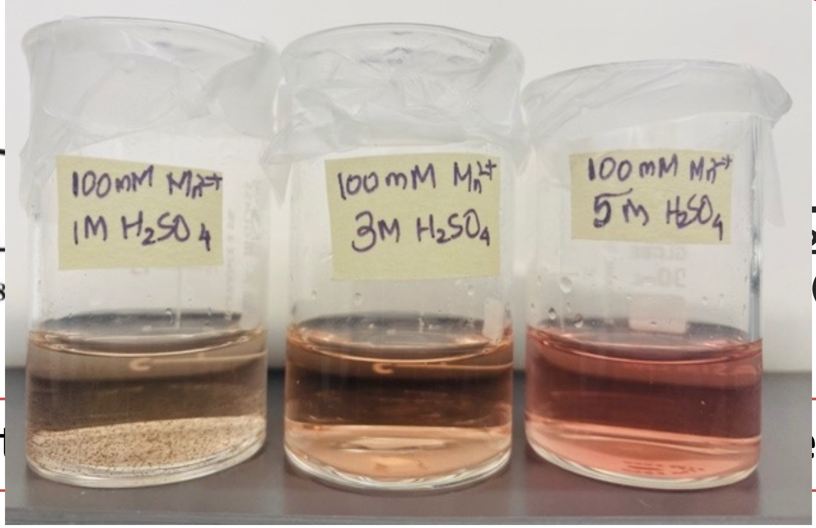
Higher yield of H_2 at higher SOC

Effect of Acid Concentration

Manganese Pourbaix Diagram



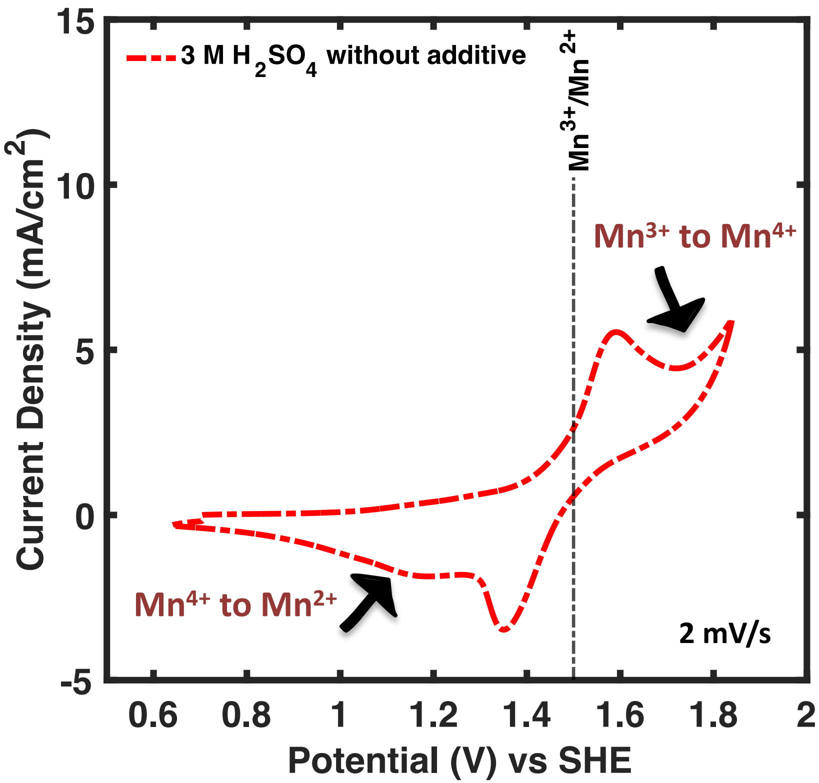


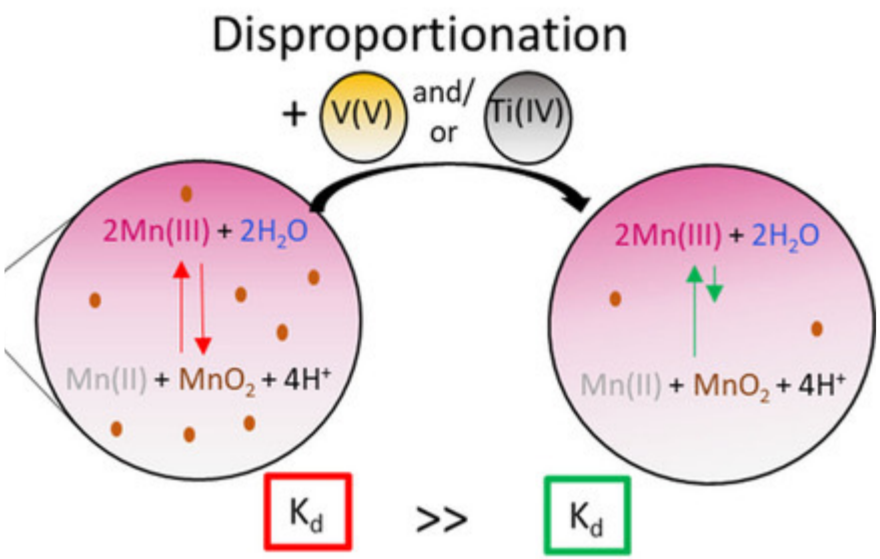


Ratio of peak current ... **r reversibility**

Yi, Chan Pei, and Siti Rohana Majid, Semiconductors-Growth and Characterization (2018): 1193

Effect of Vanadium as Additive





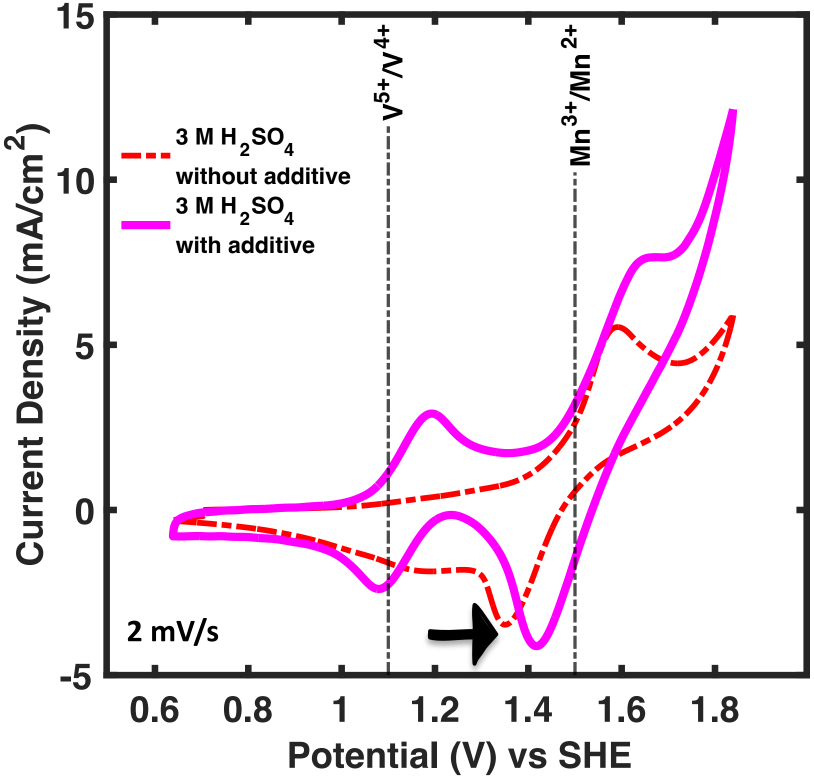
D. Reynard, S. Maye, P. Peljo, V. Chanda, H. H. Girault, S. Gentil, Chem. Eur. J. ***2020****, 26, 7250.*

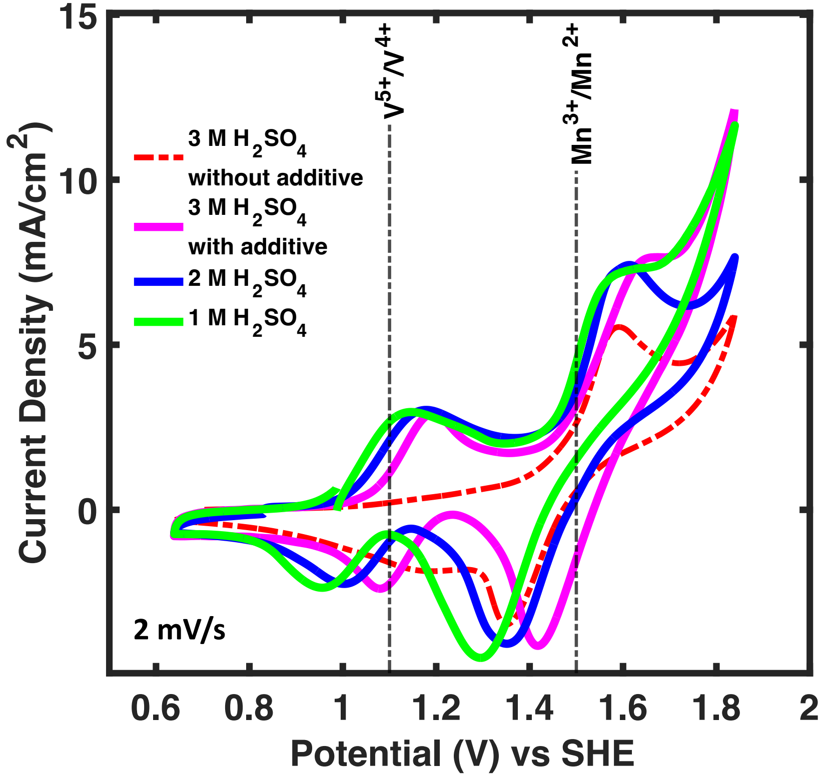
- **Capacitive currents at ~1.6 V** during oxidation suggest oxide deposition
- **Two** broad **reduction peaks** for **one oxidation peak** for Mn^{2+} to Mn^{3+}

CV experiments done at 100 mM of RM in 3M acid with Reference electrode Hg |$HgSO_4$.
Counter Electrode – Pt wire. Potential are reported vs SHE , shifted by +0.64
Graphite Plate = 21.3 cm^2

Effect of Vanadium as Additive

Stability of Redox Mediator | Electrochemical Performance | Hydrogen Generation



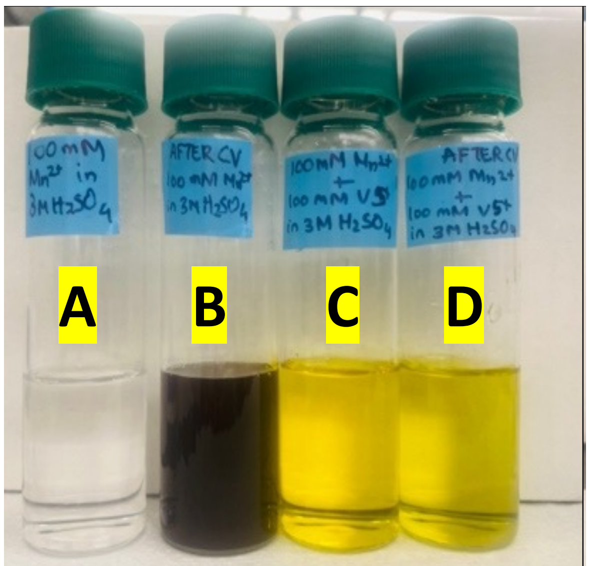


- **Positive shift in reduction potential** of Mn^{3+} to Mn^{2+}
- **Vanadium** ion possibly induces steric effects to **refrain oxo-bridge formation**

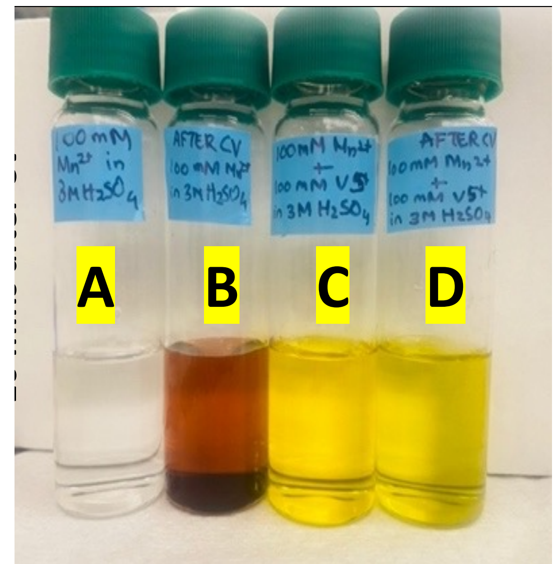
CV experiments done at 100 mM of RM in 3M acid with Reference electrode Hg |$HgSO_4$.
Counter Electrode – Pt wire. Potential are reported vs SHE , shifted by +0.64
Graphite Plate = 21.3 cm^2

Visual Stability of Manganese with Additive

Immediately after Cyclic Voltammetry



10 mins after Cyclic Voltammetry



A – Control, Pure Mn^{2+}

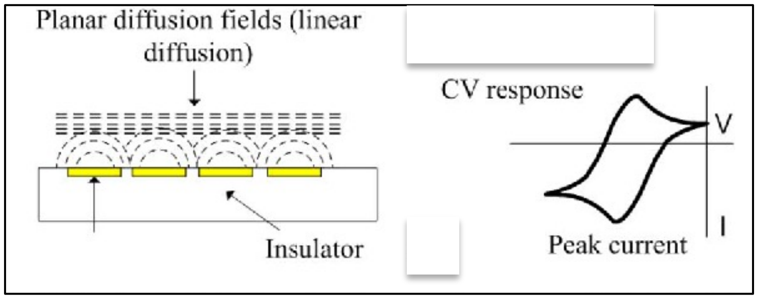
B – Mn^{3+} without Additive

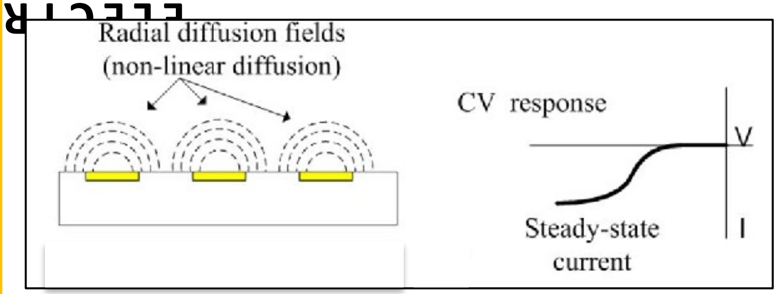
C – Mn^{2+} with Additive

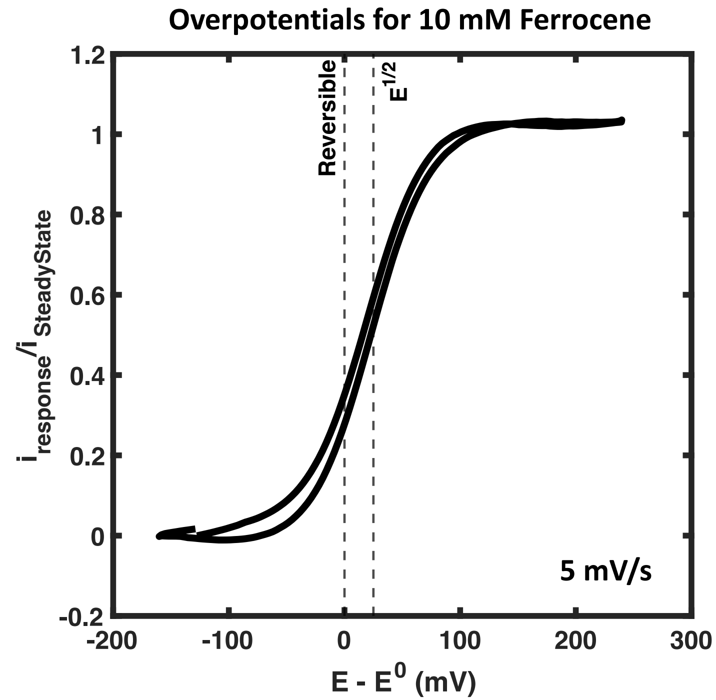
D – Mn^{3+} with Additive

- **Manganese dioxide settles after 10 minutes when without additive**
- **Vanadium** ion suppresses the large particles of Manganese dioxide

Effect of Electrode Size





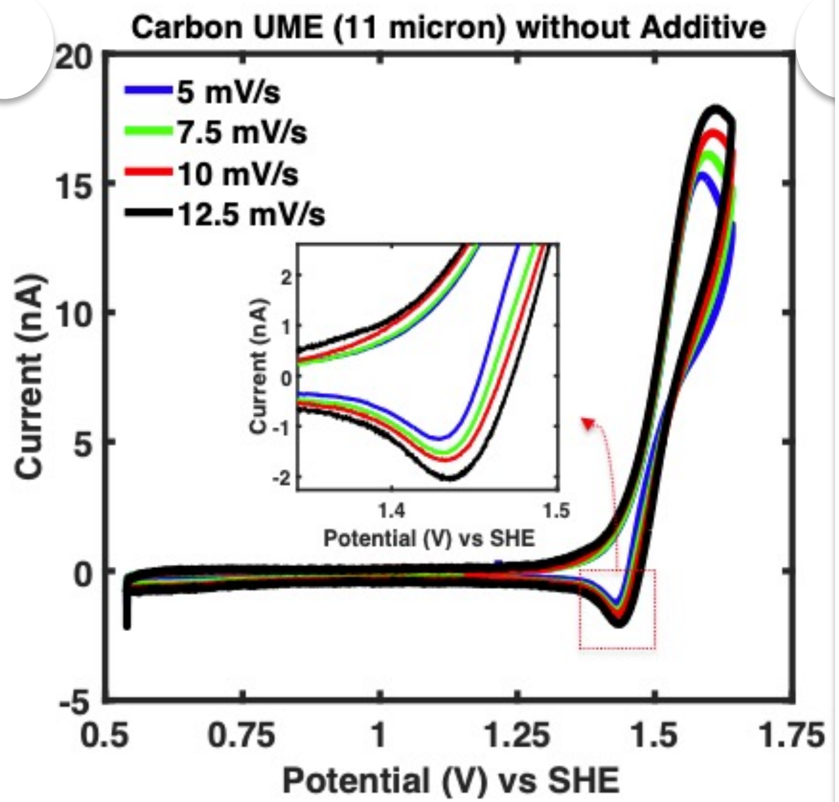


Ultramicroelectrode are robust tool to comment on **diffusion layer** and investigate **electrode-electrolyte interface phenomenon**

Ching, Stanton, et al., Journal of chemical education 71.7 (1994): 602
Hwang, S., et. al., IEEE Sensors Journal, 9, 609-615
Zoski, Cynthia G., ed. Handbook of electrochemistry. Elsevier, 2006.

Ultramicroelectrode Cyclic Voltammetry

Stability of Redox Mediator | Electrochemical Performance | Hydrogen Generation

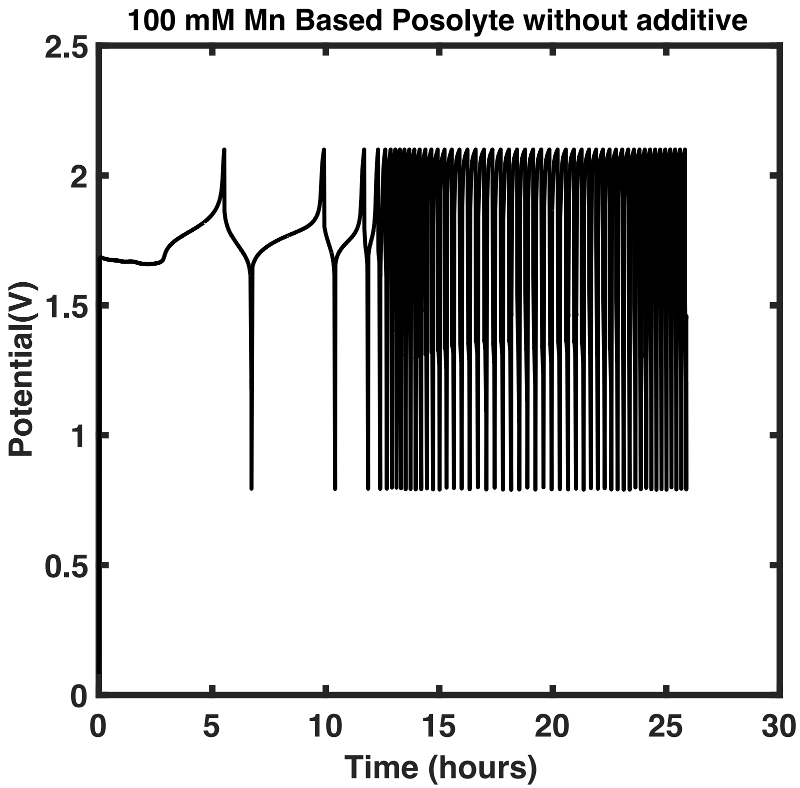


Flattening of duck shaped faradaic response in reduction branch is specific to interplay between equimolar amounts of additive V^{5+} with RM i.e., Mn^{3+} / Mn^{2+}

CV experiments done at 100 mM of RM in 3M acid with Reference electrode Hg |$HgSO_4$.
Counter Electrode – Pt wire. Potential are reported vs SHE , shifted by +0.64

Galvanostatic Cycling without Additive

Stability of Redox Mediator | **Electrochemical Performance** | Hydrogen Generation

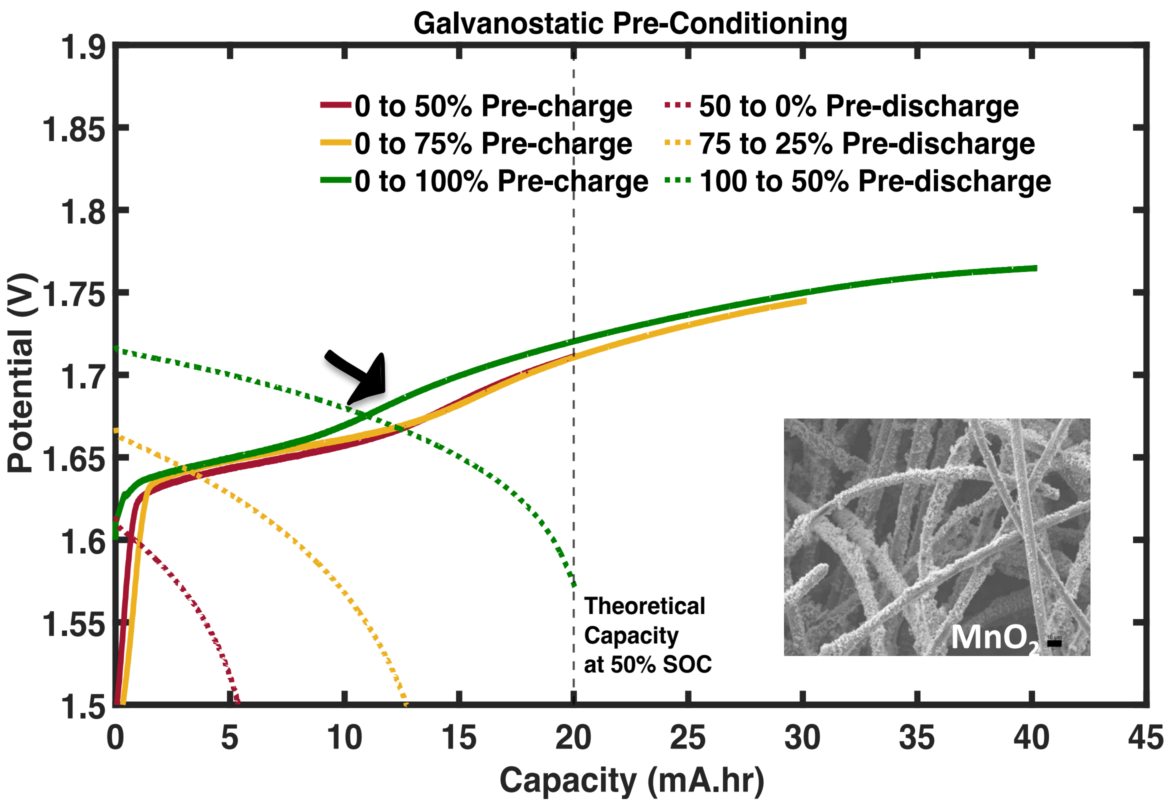


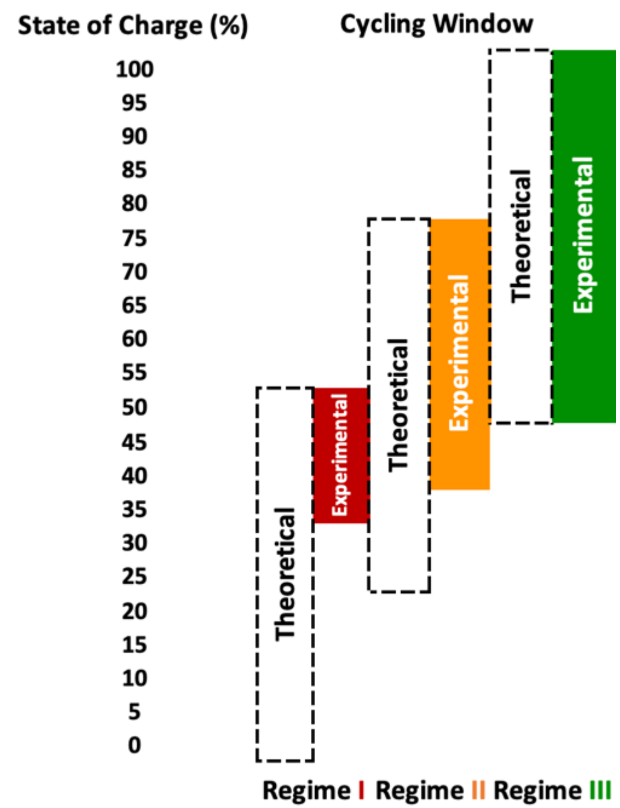
Voltage cut-offs are hit immediately as the flow fields get blocked by MnO_2 particles - displaying a poor cycling performance without additive

Experiments were performed under Nitrogen blanket for 100 mM of redox mediator with carbon felts (5 cm²) as electrodes
Current Density: 10 mA/cm² ,Flow Rate: 50 mL/min

Galvanostatic Pre-Conditioning with Additive

Stability of Redox Mediator | **Electrochemical Performance** | Hydrogen Generation



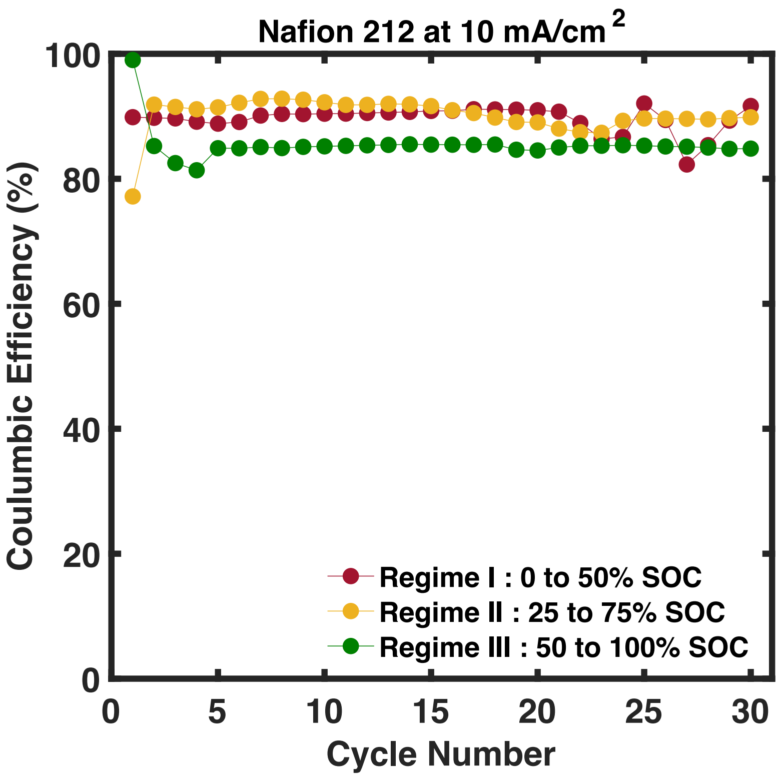


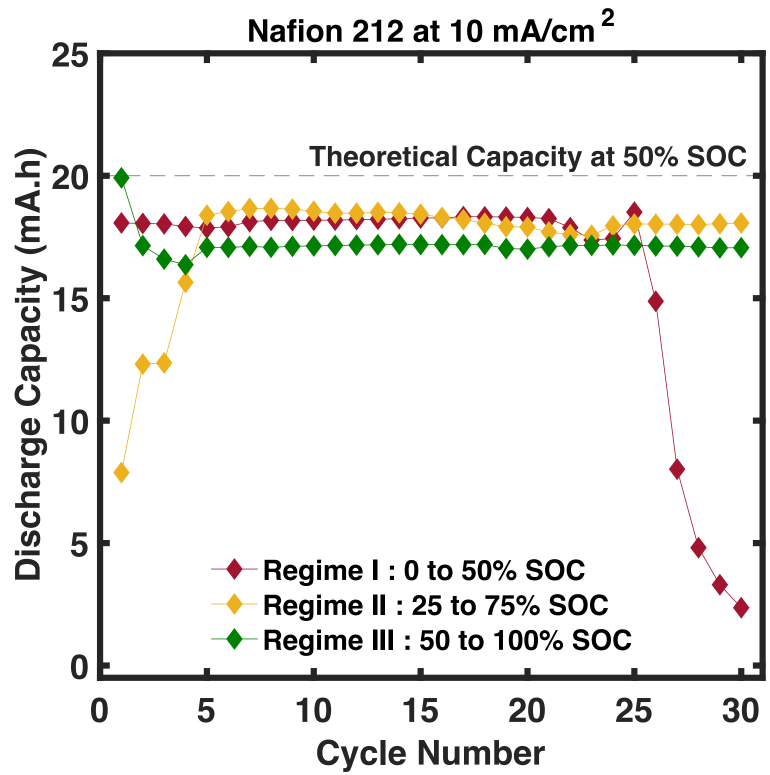
Rapid formation of MnO_2 particles in **pre-charge**
affects the **true state of charge** prior to constant current full cell cycling

Experiments were performed under Nitrogen blanket for 100 mM of redox mediator with carbon felts (5 cm^2) as electrodes
Current Density: 10 mA/cm^2 ,Flow Rate: 50 mL/min

Galvanostatic Cycling with Additive

Stability of Redox Mediator | **Electrochemical Performance** | Hydrogen Generation





Even though the experimental SOC for Regime III is near as same as theoretical; it suffers from capacity fade possibly due to thicker electrode passivation and pore blocking from MnO_2 particles

Experiments were performed under Nitrogen blanket for 100 mM of redox mediator with carbon felts (5 cm²) as electrodes
Current Density: 10 mA/cm² ,Flow Rate: 50 mL/min

Galvanostatic Cycling with Additive

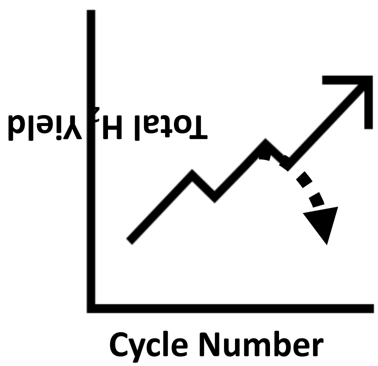
Conditions	Nafion 212			FAP 450		
	Regime 1	Regime 2	Regime 3	Regime 1	Regime 2	Regime 3
Theoretical SOC	0 to 50%	25 to 75%	50 to 100%	0 to 50%	25 to 75%	50 to 100%
CE	89.7%	90.1%	85.4%	80.2%	84.7%	86.2 %
VE	91.4%	88.8%	92.3%	94.7%	94.5%	89.5%
EE	81.9%	80.1%	78.8%	75.9%	80.0%	77.2%

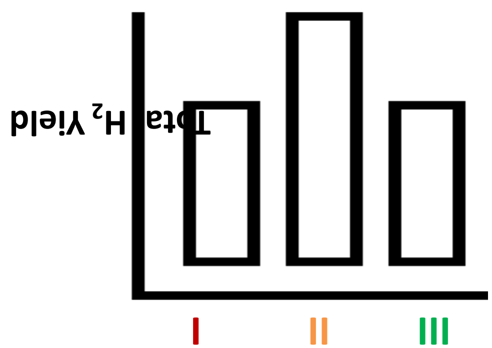
Better performance is observed with Nafion 212 as opposed to FAP 450 as it may allow the cross-over of vanadium ions for Mn^{3+} steric stabilization.

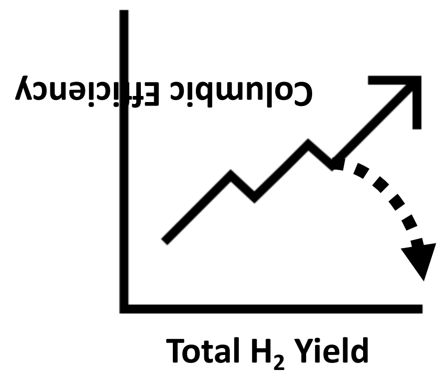
Experiments were performed under Nitrogen blanket for 100 mM of redox mediator with carbon felts (5 cm^2) as electrodes
Current Density: 10 mA/cm^2 ,Flow Rate: 50 mL/min

Hydrogen Generation

1. What is the maximum H_2 yield for a fixed capacity retention **?**
2. Which operating SOC window gives maximum H_2 yield **?**
3. What is the affect of Mn^{3+} disproportionation reaction on total H_2 yield **?**

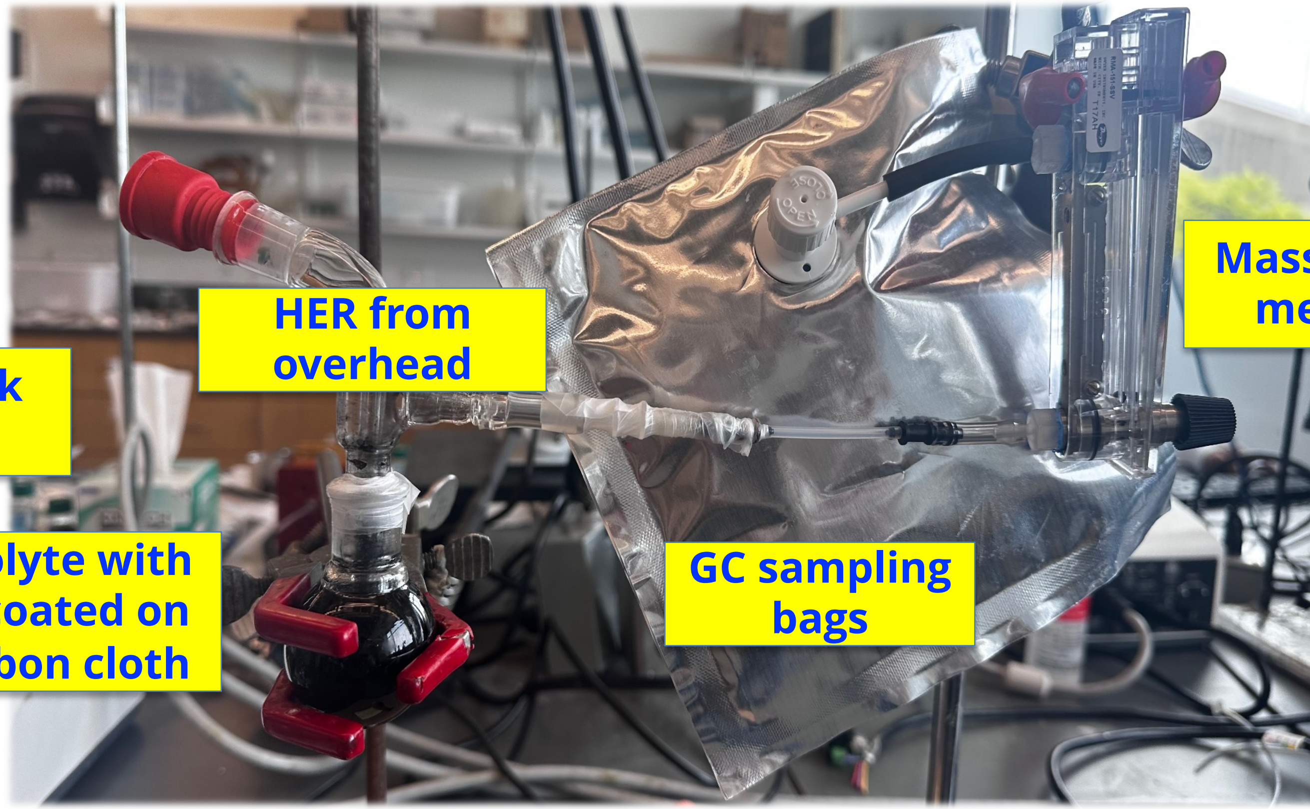






Regime I – Low SOC charging depth (0 to 50%)
Regime II – Moderate SOC charging depth (25 to 75%)
Regime III – High SOC charging depth (50 to 100%)

Hydrogen Generation



Rudimentary set-up to collect Hydrogen gas

Electrocatalyst – 40 wt% Pt on Vulcan coated on Carbon Cloth

H_2 Evolution Reaction Electrocatalyst

Commercial Pt Ink composition (40 wt% on Vulcan)
i.e., 30 mg/g Pt + 10 mg/g Nafion

1. Pt Ink was drop casted & coated on Carbon Cloth (1 cm x 1 cm) using blade
2. Dried in oven at 50 °C overnight (no vacuum)

Carbon cloth weight	Carbon Cloth weight *After overnight drying*	Net weight of Platinum Ink	Platinum Loading
(mg)	(mg)	(mg)	(mg/cm^2)
61.8	**148.6**	**86.8**	**~ 2.5**

Electrocatalyst – 40 wt% Pt on Vulcan coated on Carbon Cloth

Chemical Discharge of V^{2+}

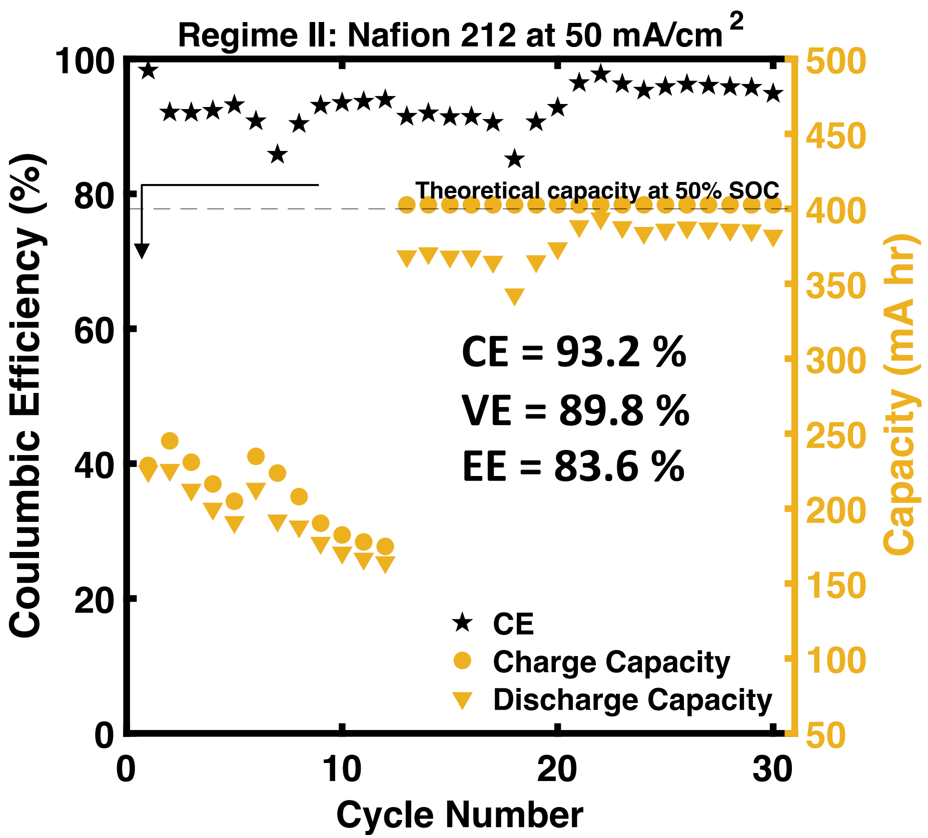
Stability of Redox Mediator | Electrochemical Performance | **Hydrogen Generation**

After 30 cycles - 30 mL ~ 75% SOC V^{2+}

Catholyte : 0.5 M Mn^{2+} with 0.5 M V^{5+} (60 mL) = 804 mA.hr

Anolyte : 1 M V^{3+} (30 mL) = 804 mA.hr

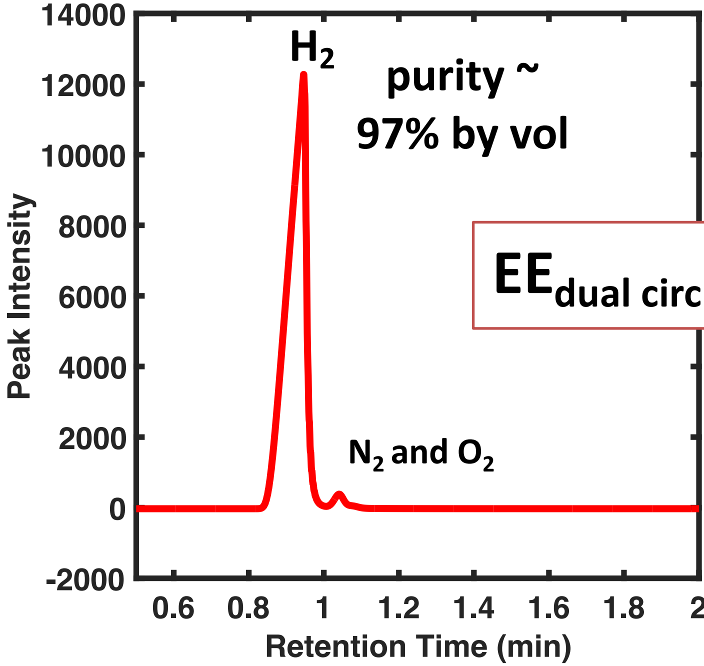
Regime II : (25 to 75%) at 50 mA/cm² and 50 mL/min



Hydrogen Gas Chromatography

After 30 cycles - 30 mL ~ 75% SOC V^{2+} was obtained at **1.83** Volts

Regime II : 25 to 75% Qualitative



$EE_{dual\ circuit\ RFB}$ =

CE = 93.2 %

VE = 89.8 %

EE_{RFB} = 83.6 %

Purity ~ 97 %

$EE_{dual\ circuit\ RFB}$ ~ 68 %

Future Work

Stability of Redox Mediator | Electrochemical Performance | **Hydrogen Generation**

1. Develop a better way to coat Platinum ink on carbon cloth because
   - Complete discharge of 30 mL V^{2+} to V^{3+} takes about a **day**.
   - Catalyst delamination was observed
   - Kinetics is perhaps slow?
   - Flow rate dropped quickly < 10 mL/min within seconds.

1. Integrate the 3-way valves on positive side for OER for simultaneous water splitting

1. Install the in-line digital mass flow meter

1. Integrate Gas Chromotography for operando quantification

Key Findings

1) Proof of concept was developed using asymmetric cell cycling of V-Mn: redox mediated water electrolysis concept provides a one stop solution for energy dense renewable systems

2) **Mn^{2+}** is identified as the suitable catholyte redox mediator to drive water oxidation but is limited by disproportionation reaction

3) **V^{5+}** as an additive fine tunes the stability of Mn^{3+} in aqueous media

4) Ultra microelectrode voltammetry is a useful diagnostic tool to understand interface layer for complex redox systems

5) True State of Charge during pre-conditioning is altered by rapid MnO_2 formation and requires further optimization

Acknowledgements

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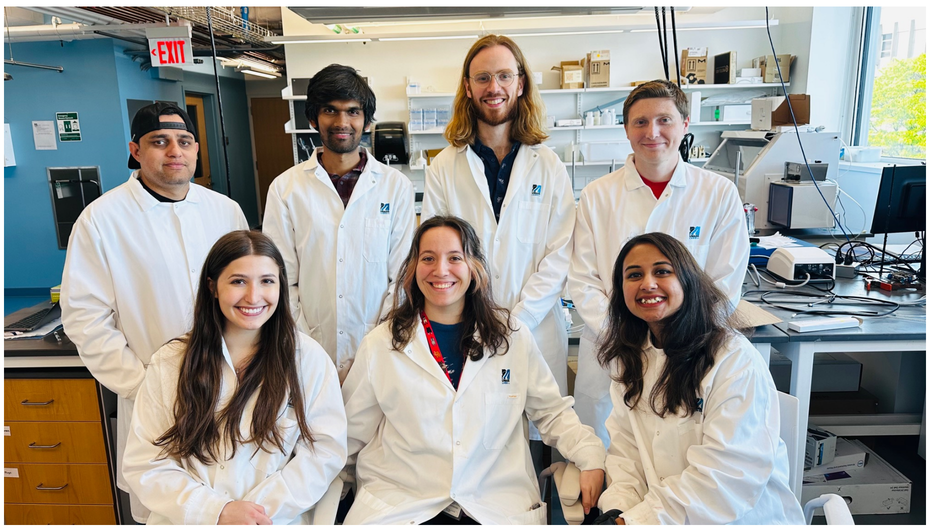

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Dual-Layer Energy Storage:

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