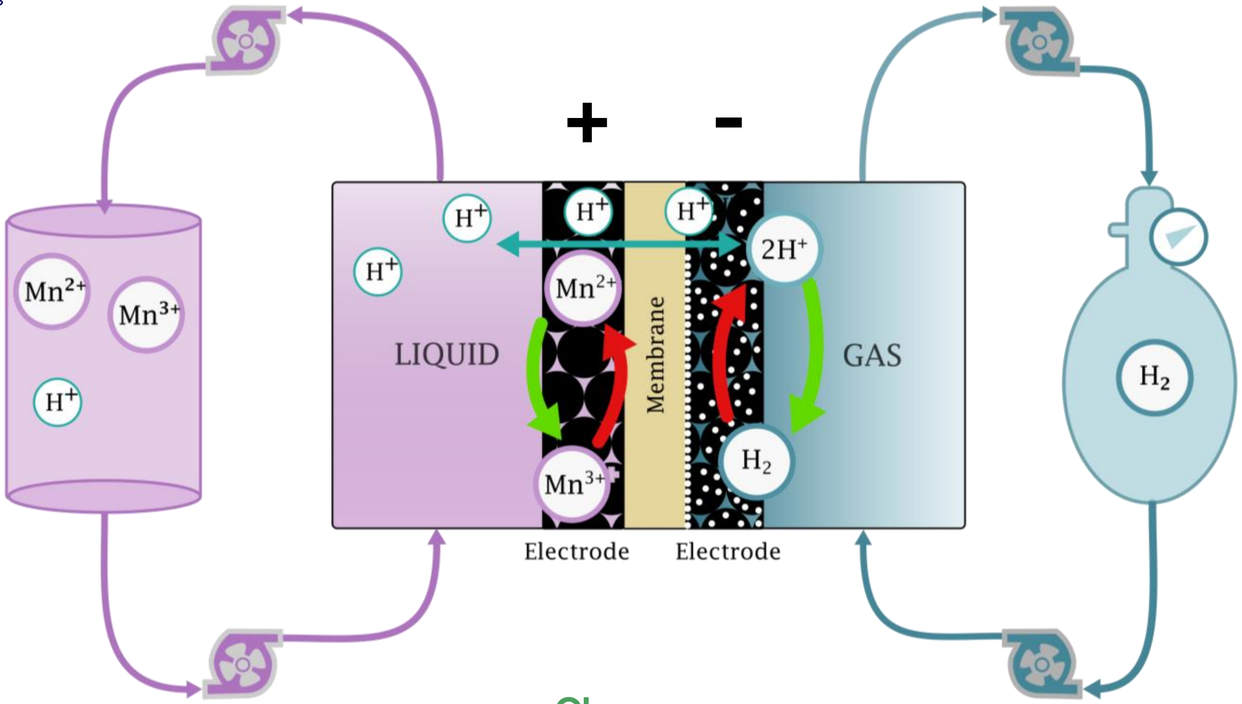
# A Systematic Study on the Performance and Stability of Hydrogen-Manganese Flow Battery

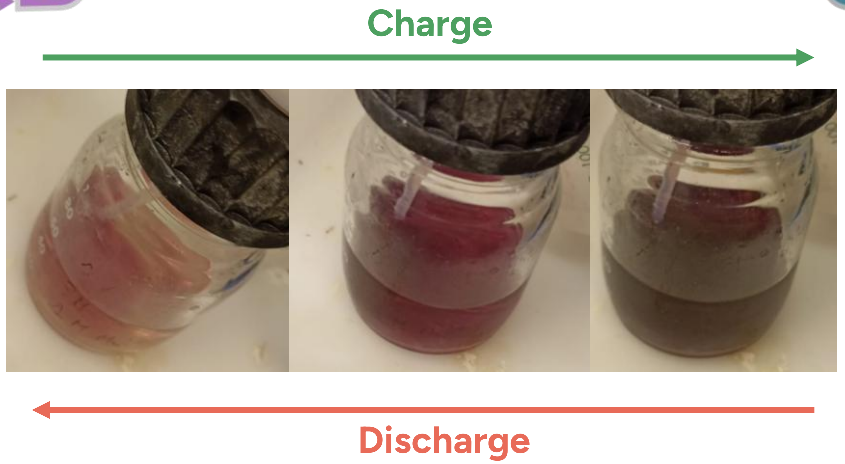
Erlantz Villar[1*], Rakel Wreland Lindström[1], Amirreza Khataee[1]

[1]Applied Electrochemistry, KTH Royal Institute of Technology, Stockholm, Sweden

Email: erlantz@kth.se

# Why Hydrogen-Manganese?




Charge / Discharge

$$Mn^{2+} \rightleftharpoons Mn^{3+} + e^-$$ $E^0 = 1.51$ V

Charge / Discharge

$$2H^+ + 2e^- \rightleftharpoons H_2$$ $E^0 = 0$ V

## Advantages:

- High cell voltage of 1.51 V
- Manganese is abundant and low-cost (~2 €/kg Mn vs ~12 €/kg V)
- Fast kinetics of the hydrogen reaction
- The crossover can be collected on the anode side and pumped back

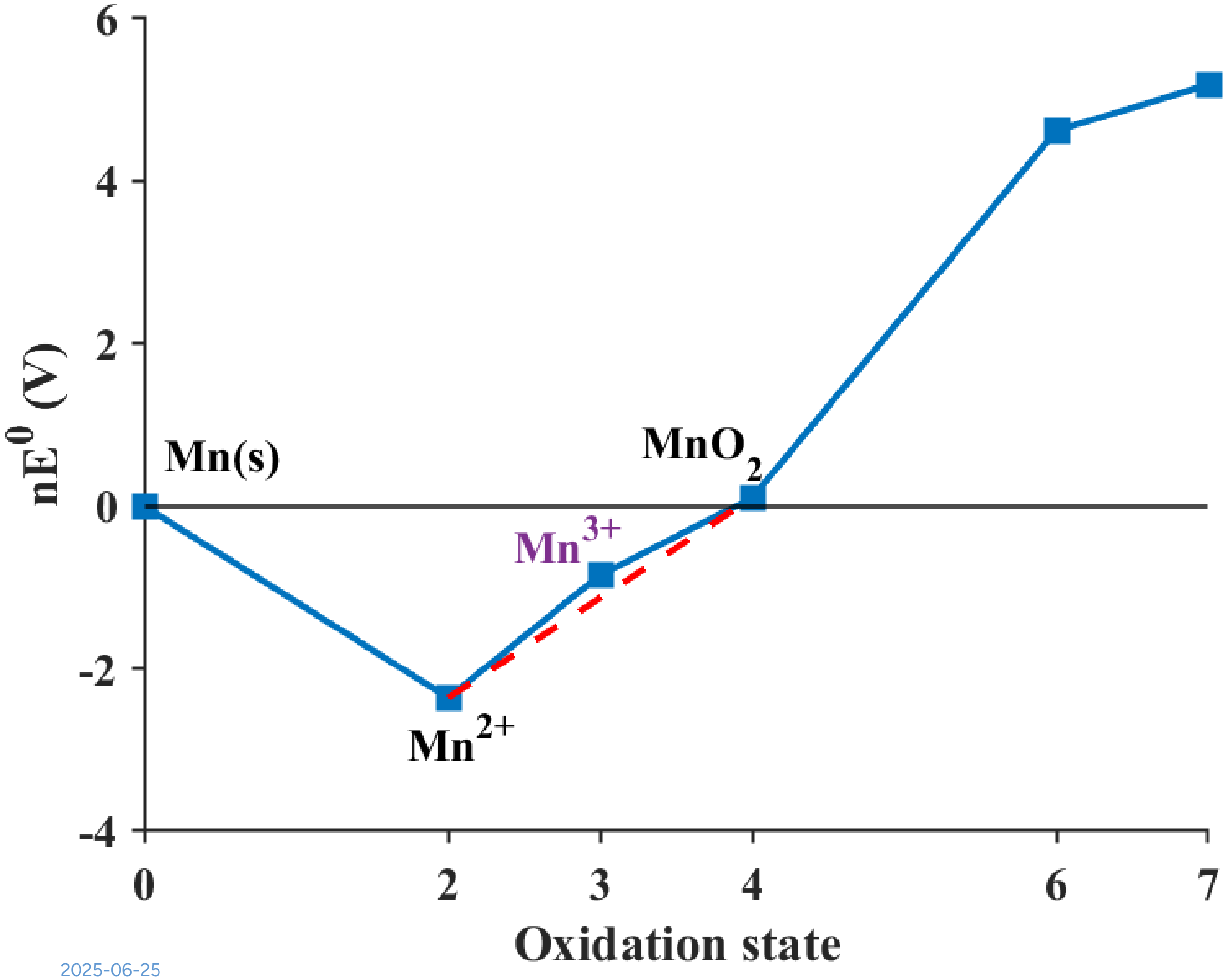


J. Rubio-Garcia, A. Kucernak, D. Zhao, D. Li, K. Fahy, V. Yufit, N. Brandon, and M. Gomez-Gonzalez, Journal of Physics: Energy, 1, 015006 (2018).

# Hydrogen-manganese challenge

Charge

$Mn^{2+} \rightarrow Mn^{3+} + e^{-}$  $E^0 = 1.51$ V

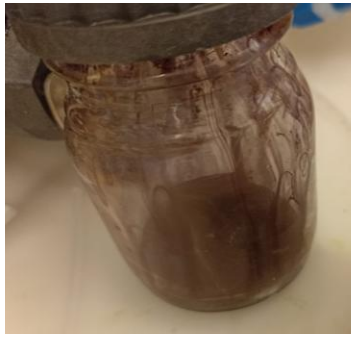



Disproportionation reaction:

$$2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2(s) + 4H^+$$

Challenges:

- Precipitation (Clogging)
- $Mn^{3+}$ loss (Capacity loss)



Additive ($TiO^{2+}$)

- Partial solution
  - $MnO_2$(s) smaller
  - Can be reduced
  - No clogging
- Disproportionation still takes place

# Purpouse of the study

## <u>Motivation</u>

❖ Can we suppress disproportionation by optimizing operational parameters?
- Voltage window
- Current density
- Rest time

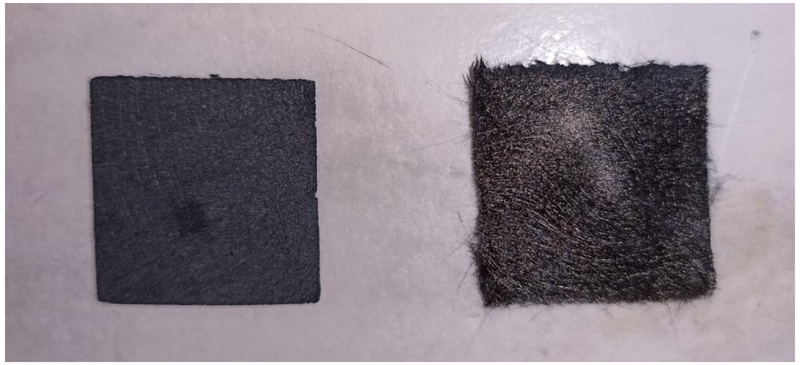
## <u>Goals</u>

❖ How do operational parameters affect:
- Performance
- Disproportionation

Even with $TiO^{2+}$

- Particles in the bottom of the tank
- Suspension of particles in the electrolyte

**Before cycling** **After cycling**

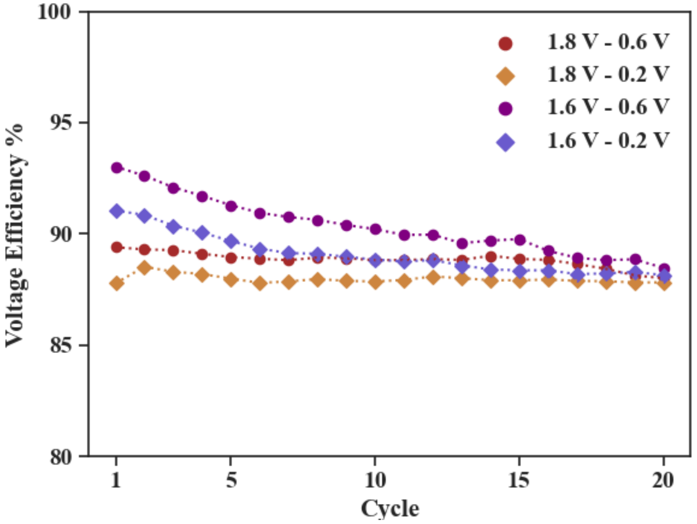


- Electrode is "damaged"

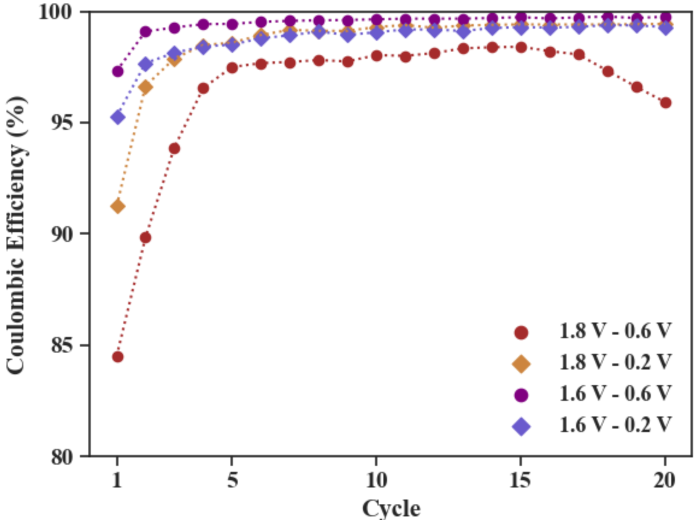
**Disproportionation must be controlled!!!**

# Cutoff voltage effect (0.6 V vs 0.2 V & 1.8 V vs 1.6 V)

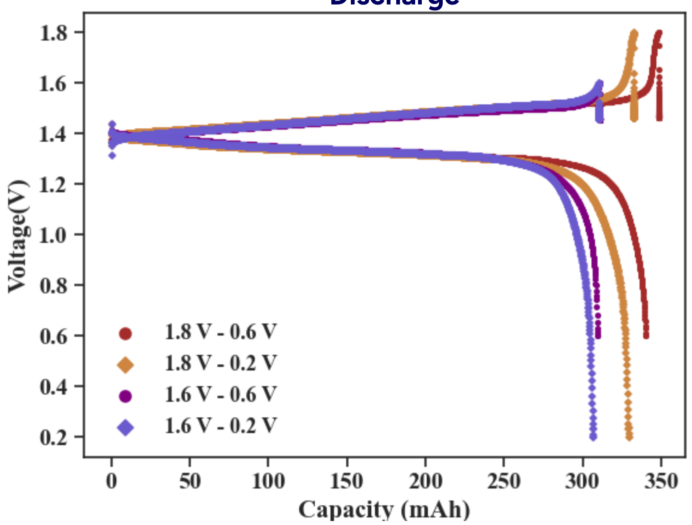
**VE**




**CE**




**$Q_{Discharge}$**




**Lower cutoff voltaje**

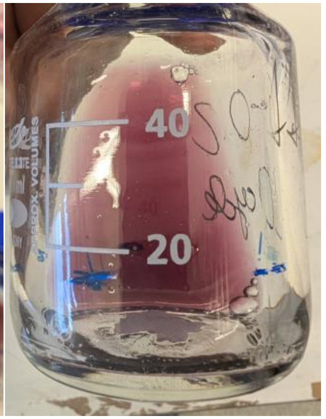
- Small effect
- 0.6 V slightly better

**Upper cutoff voltaje**

- 1.8 V:
  - Lower VE & CE
  - Higher capacity
- 1.6 V
  - Higher VE & CE
  - No particles after discharge

**1.8 V**

**1.6 V**



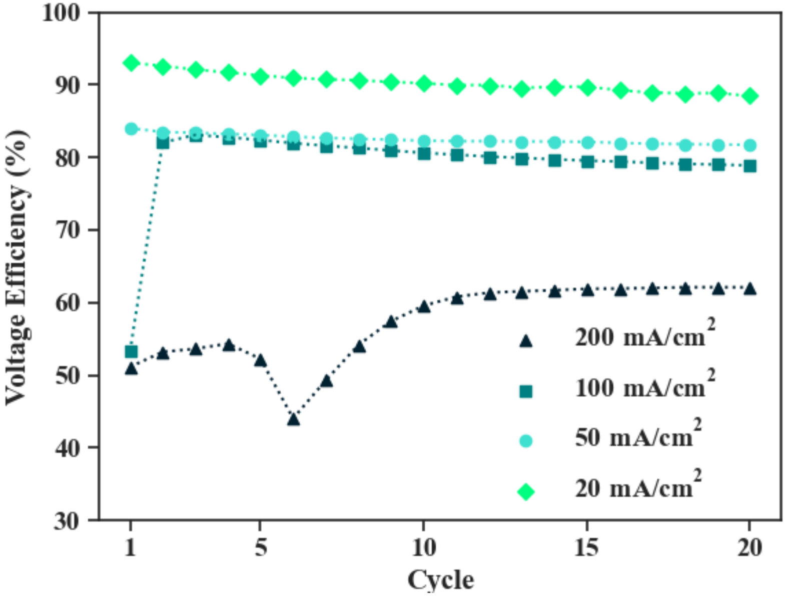

**1.6 V – 0.6 V optimal**

**$MnO_2$ ↓ Efficiency ↑ Lifetime ↑**

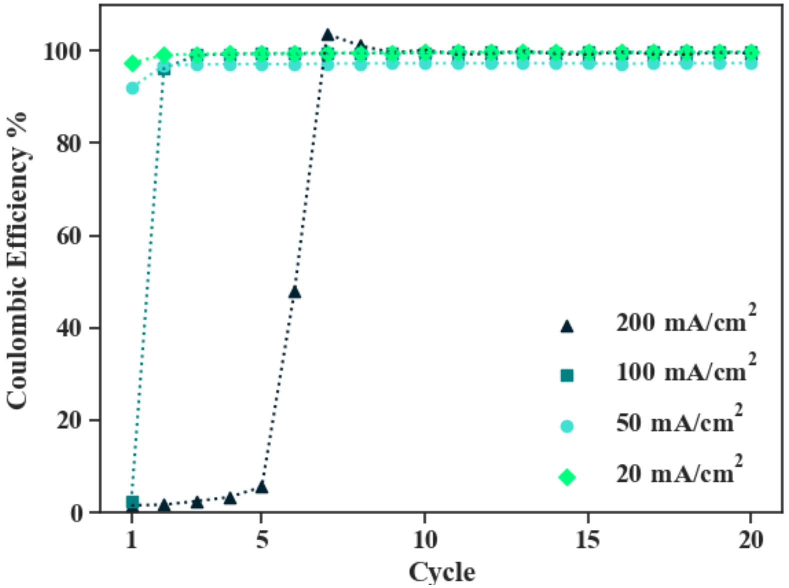
# Current density effect

(1.6 V – 0.6 V) $Q_{theoretical}$= 350 mAh

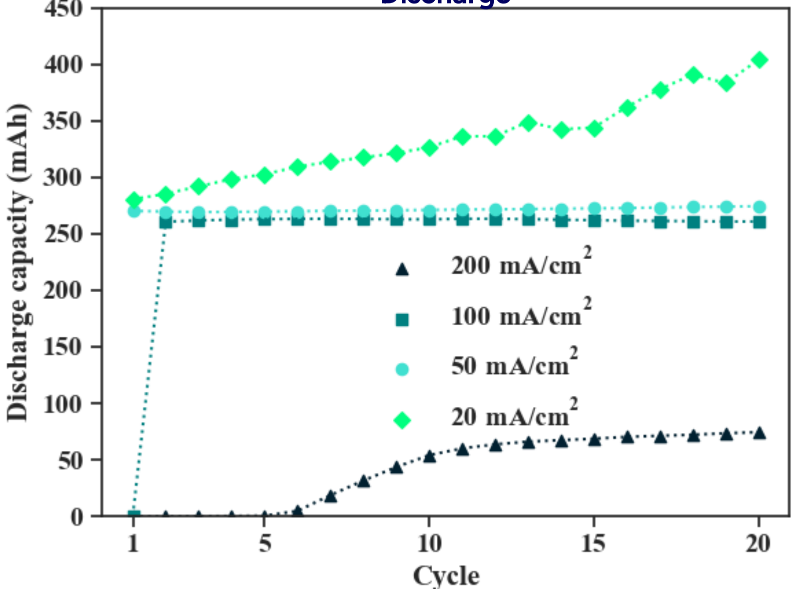
VE




CE




$Q_{Discharge}$




- Stable performance at 20-100 mA cm$^{-2}$
- Reversible reaction
- Some activation cycles needed at >= 100 mA cm$^{-2}$
- Capacity increase at < 50 mA cm$^{-2}$

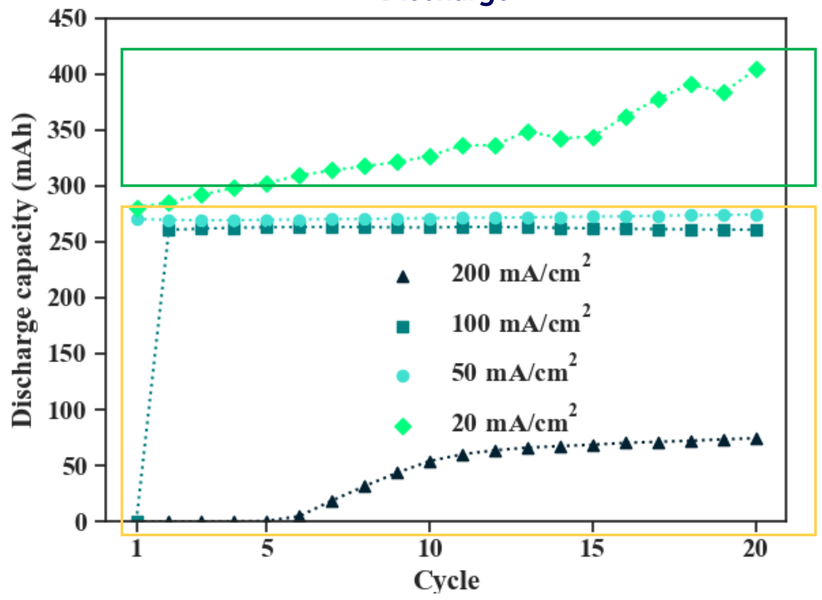
## Activation steps

- Electrochemical activation
  - Mass transport
- During cycling: Build-up of redox species

# Current density effect

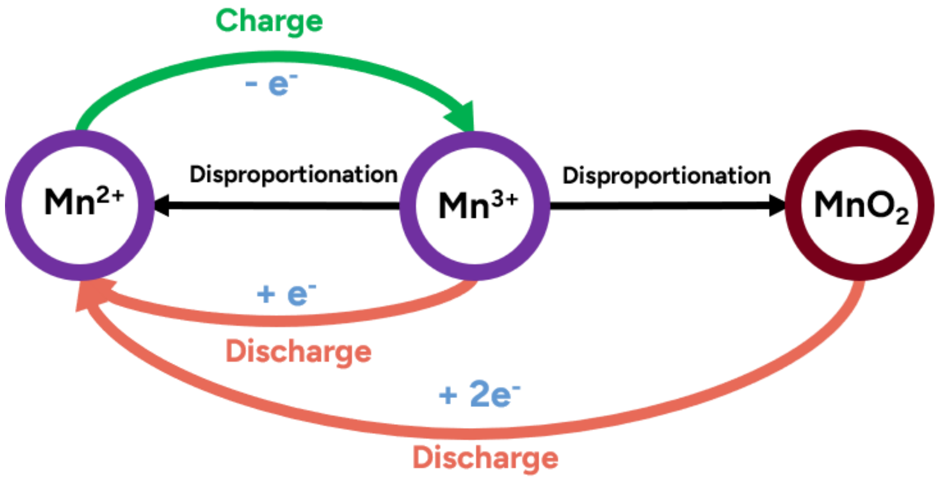
($1.6\ V - 0.6\ V$)

$Q_{Discharge}$




Capacity increase (<50 mA $cm^{-2}$)

**Disproportionation:** $2Mn^{3+} + H_2O \rightarrow Mn^{2+} + \mathbf{MnO_2(s)} + 4H^+$




**Case 1: Fast charge (>= 50 mA $cm^{-2}$)**

- No disproportionation
- No extra $Mn^{2+}$ charged

**Case 2: Slow charge (< 50 mA $cm^{-2}$)**

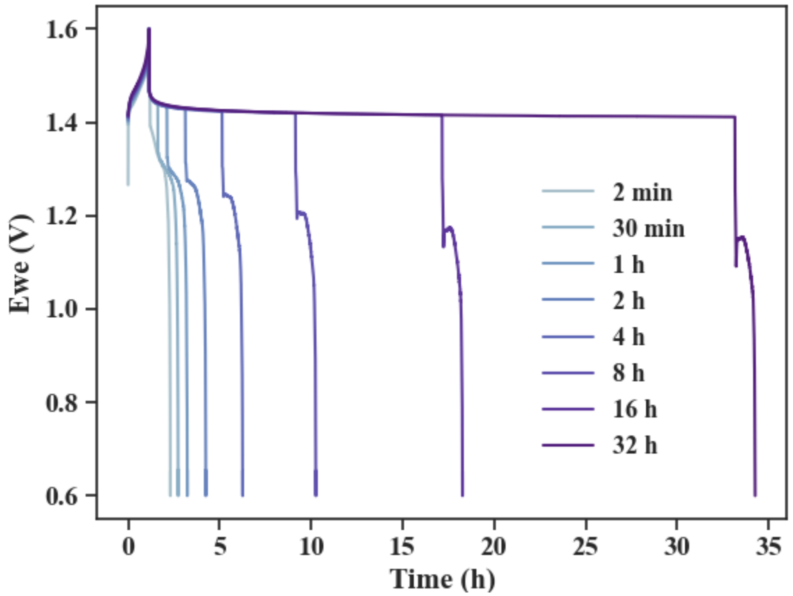
- Disproportionation
- Extra $Mn^{2+}$ charged
- Extra capacity from $MnO_2$

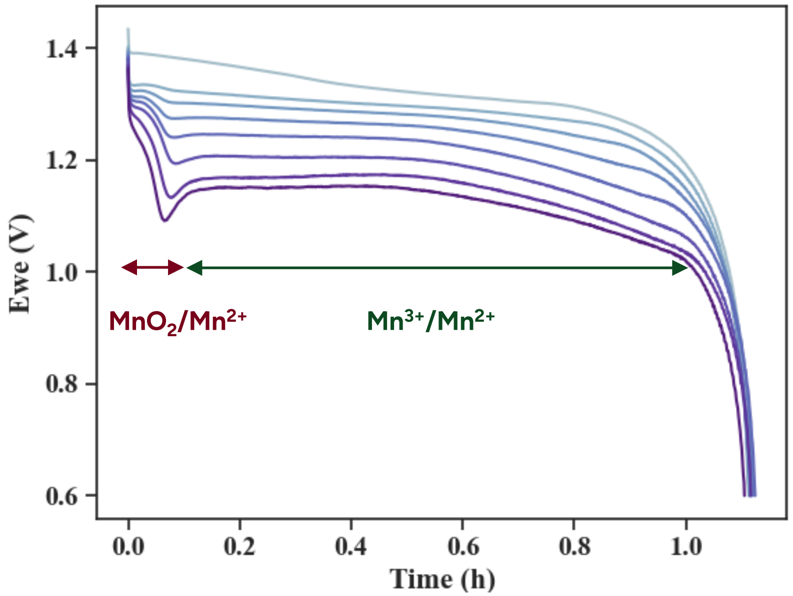
**Hypothesis**

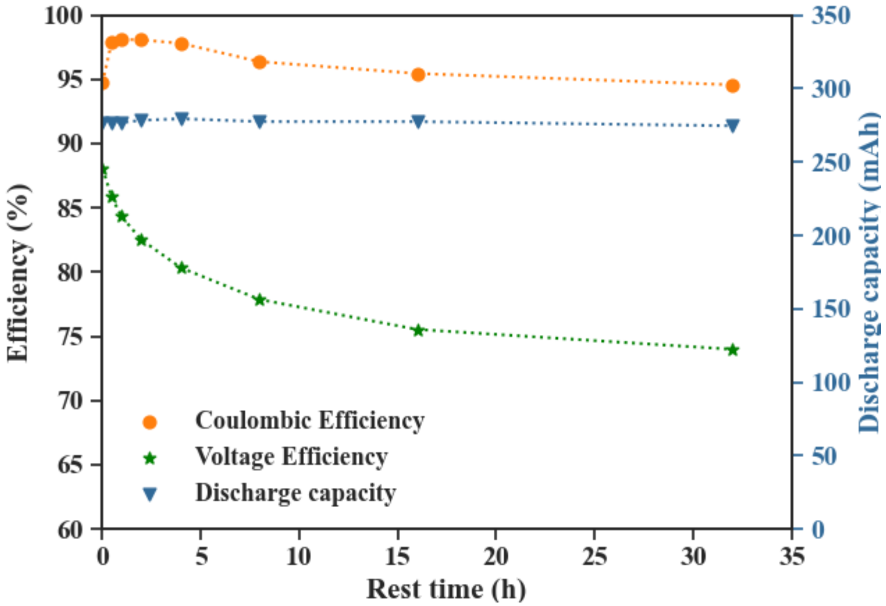
Charging time affects the disproportionation reaction

# Rest time between charge and discharge (1.6 V – 0.6 V)

Charge (50 mA $cm^{-2}$) → Rest time → Discharge (50 mA $cm^{-2}$)




- VE drops after 30 min rest time
- CE quite constant (Small side reactions)
- Capacity constant (Reversible $MnO_2$)

**Rest time ↑**
**$MnO_2$ ↑ Efficiency ↓ Lifetime ↓**

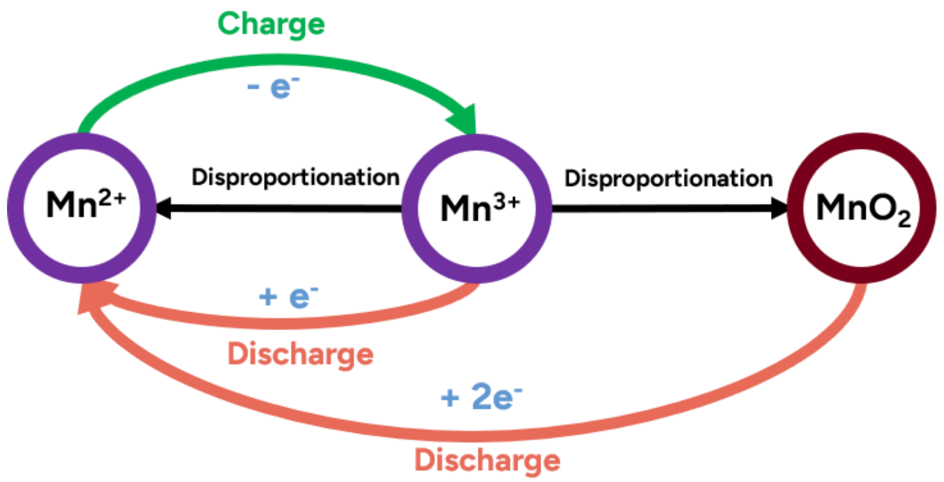
# Conclusions

- **Disproportionation can be controlled by operational parameters**
- Cutoff voltage:
  - Upper cutoff has the biggest impact

**1.6 V – 0.6 V optimal**
**$MnO_2$ ↓ Efficiency ↑ Lifetime ↑**

- Current density:
  - Optimal performance range 50 – 100 $mA/cm^2$
  - At <50 $mA/cm^2$ capacity increases over cycles
    - New possibilities of design
- Rest time:
  - Reversible $MnO_2$ reaction

**Rest time ↓**
**$MnO_2$↓ Efficiency ↑ Lifetime ↑**



# Acknowledgements

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KTH

VETENSKAP OCH KONST