Zinc Batteries for Grid-Scale Energy Storage

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Grid-scale battery energy storage

- Grid-scale energy storage systems converts energy collected from the grid or a power plant into a storable form for later use
- Storage systems are key for grid stability and integration of variable renewable energy sources
- Conventional energy storage technologies are limited by geographical constraints (hydroelectric, compressed air), operational safety concerns and high self-discharge rates (flywheels), and potential lag time between demand and energy supply
- Grid-scale electrochemical energy storage systems (GSEESSs) are not geographically constrained, can be designed safely and with extremely low self discharge rates, and have immediate response times for demand
- GSEESSs stabilize the grid through peak shaving and load leveling, voltage and frequency regulation, and emergency power supply
- **Li-ion represents a significant portion of installed GSEESSs, however due to lifetime, safety, and raw material sourcing concerns, alternative technologies are highly desirable**

Grid Scale Electrochemical Energy Storage

Beyond Li-Ion Batteries for Grid-Scale Energy Storage

Authors and Affiliations:
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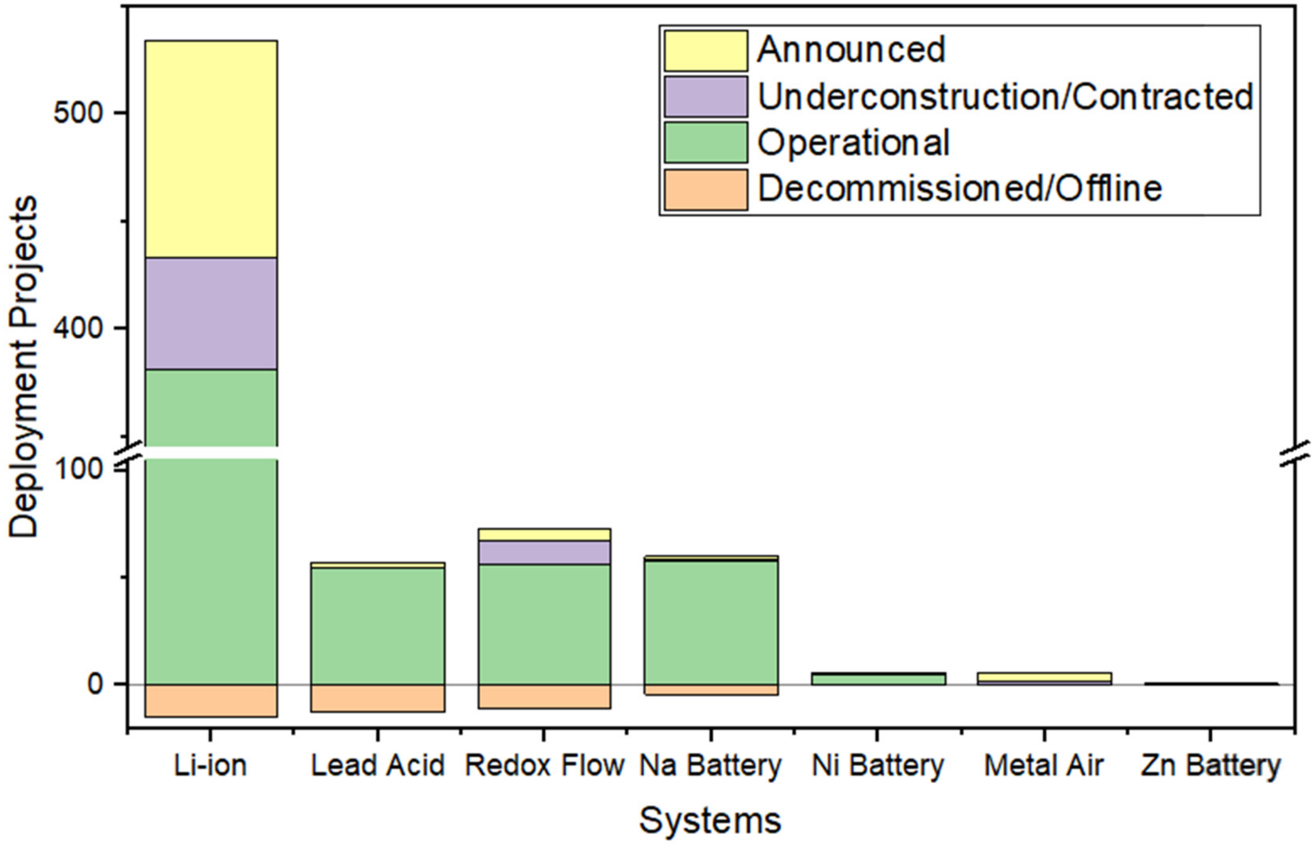
Abstract:
In order to improve resiliency of the grid and enable integration of renewable energy sources into the grid, the utilization of battery systems to store energy for later demand is of the utmost importance. The implementation of grid-scale electrical energy storage systems can aid in peak shaving and load leveling, voltage and frequency regulation, as well as emergency power supply. Although the predominant battery chemistry currently used is Li-ion; due to cost, safety and sourcing concerns, incorporation of other battery technologies is of interest for expanding the breadth and depth of battery storage system installations. Here we discuss existing technologies beyond Li-ion battery storage chemistries that have seen grid-scale deployment, as well as several other promising battery technologies, and analyze their chemistry mechanisms, battery construction and design, and corresponding advantages and disadvantages.

Contents

Elements in Grid Scale Storage. Cambridge Elements, Cambridge University Press, 2022.
Editors: Babu Chalamala, Arya Thampi. DOI: https://doi.org/10.1017/9781009030359

GSEESS deployment

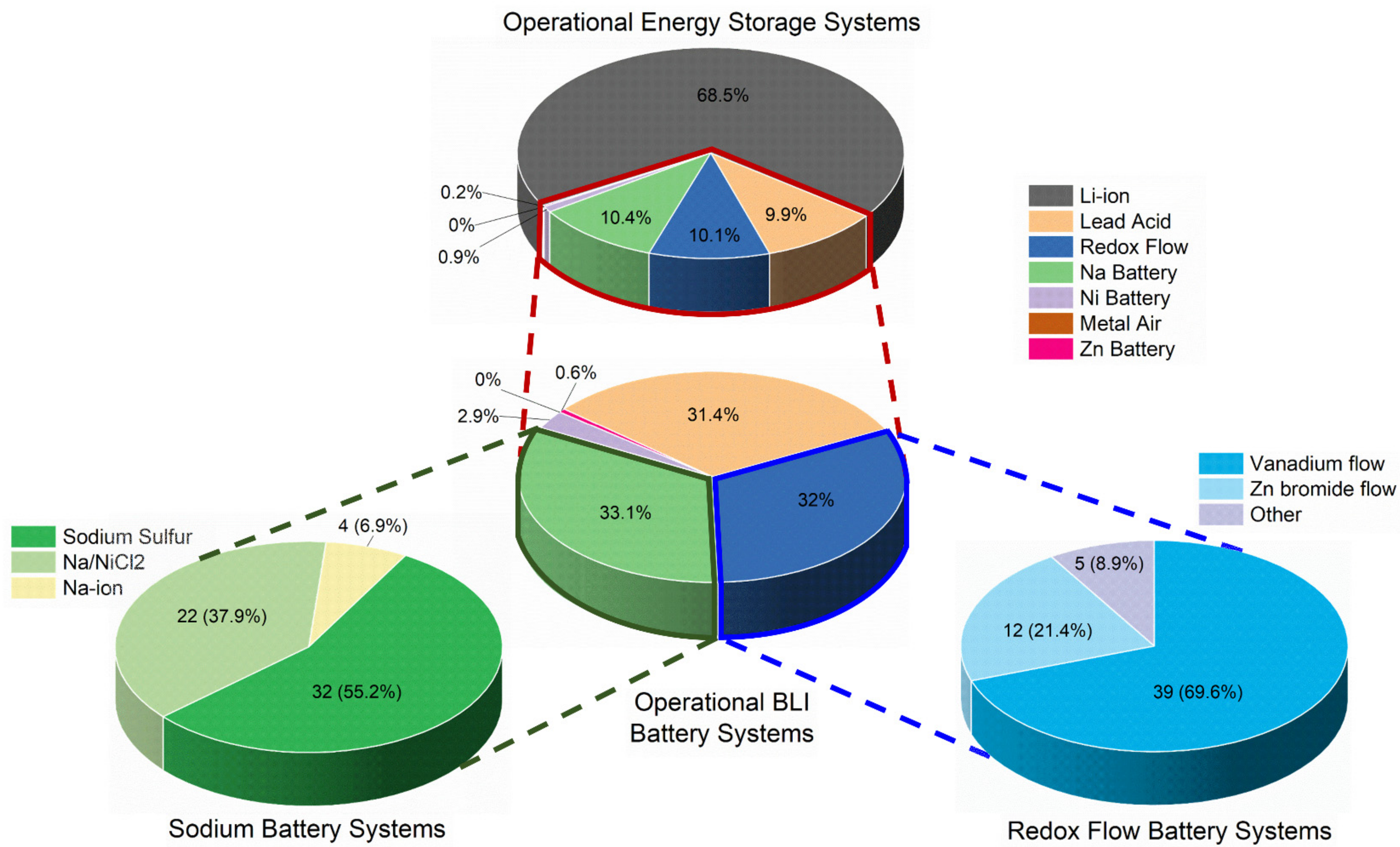
- Due to lifetime, safety, and raw material sourcing concerns, alternative technologies are desired
- Older technologies (lead acid, high temperature NaS) make up the largest non-Li-ion systems, but many of these older systems are being decommissioned
- Redox flow systems due to their scalability have seen a large increase in interest in recent years and now make up ~10% of the operational systems



"DOE OE Global Energy Storage Database," ed: National Technology & Engineering Sciences of Sandia, 2020.

J. Hernández, I. Gyuk, C. Christensen, *2016 IEEE International Conference on Power System Technology (POWERCON)*, 2016, pp. 1-6,

"Distributed Energy Resources Database," ed: New York State Energy Research and Development Authority, 2020.


Operational Energy Storage Systems
68.5%
0.2%
0%
0.9%
10.4%
10.1%
9.9%
Li-ion
Lead Acid
Redox Flow
Na Battery
Ni Battery
Metal Air
Zn Battery
0%
0.6%
2.9%
31.4%
33.1%
32%
Vanadium flow
Zn bromide flow
Other
Sodium Sulfur
Na/NiCl2
Na-ion
4 (6.9%)
22 (37.9%)
32 (55.2%)
5 (8.9%)
12 (21.4%)
39 (69.6%)
Operational BLI Battery Systems
Sodium Battery Systems
Redox Flow Battery Systems

Potential Advantages of Zn Based Batteries

Relative to Li based batteries, Zn based batteries have the potential to be safer, less expensive, and have higher volumetric capacity

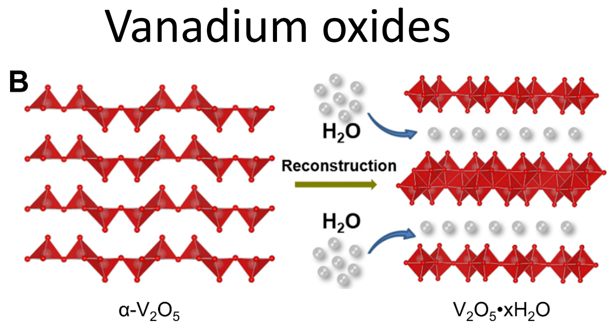
Property	Mg	Li	Zn
Ionic Radius (pm)	86	90	88
Voltage vs. S.H.E.	-2.37	-3.04	-0.76
Elemental Abundance (ppm in earth's crust)	2.8×10^4	20	78
Volumetric Capacity (mAh/cm^3)	3833	2046	5854
Gravimetric Capacity (mAh/g)	2205	3862	820
Volumetric energy (mWh/cm^3)	9084	6138	4449
Gravimetric energy (mWh/g)	5226	11586	623
$/lb	$1.12	$28	$1.16

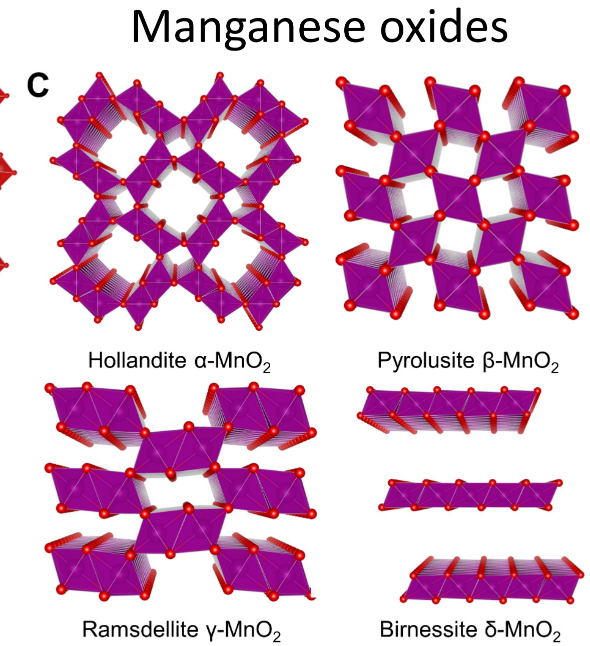
M.H. Huie, D.C. Bock, E.S. Takeuchi, A.C. Marschilok, K.J. Takeuchi*, *Coordination Chemistry Reviews,* **2015,** *287,* 15-27.

Rechargeable aqueous zinc batteries (RAZB)

The Zn^{2+} ion's increased electrostatic interactions causes challenges for deintercalation

For this reason, vanadium and manganese oxides with large layers and tunnel structures are affective cathodes





- Vanadium oxides (ex. V_2O_5, V_3O_8) offer very high-rate capabilities (>4A/g) and high capacities (>300 mAh/g), but have low voltages (<1V) and are known to dissolve over time and passivate the Zn anode
- Manganese oxides (ex. MnO_2, $K_{0.8}Mn_8O_{16}$) have higher voltages (1.3-1.4V) but lower capacities (200-300 mAh/g). High-capacity retention over thousands of cycles has been observed at reasonable rates (1-2A/g)
- MnO_2 is also known to dissolve over time, however the addition of 0.1 M $MnSO_4$ is effective at suppressing Mn dissolution which allows for the long cycle lives

Grid-scale development and installation is already underway using Zn/MnO_2 batteries in an alkaline electrolyte with a 1 MWh system in construction for the City University of New York

G. Fang, J. Zhou, A. Pan, S. Liang, *ACS Energy Letters,* vol. 3, no. 10, pp. 2480-2501, **2018.**

B. Y. Tang, L. T. Shan, S. Q. Liang, J. Zhou, *Energy & Environmental Science,* vol. 12, no. 11, pp. 3288-3304, **2019.**

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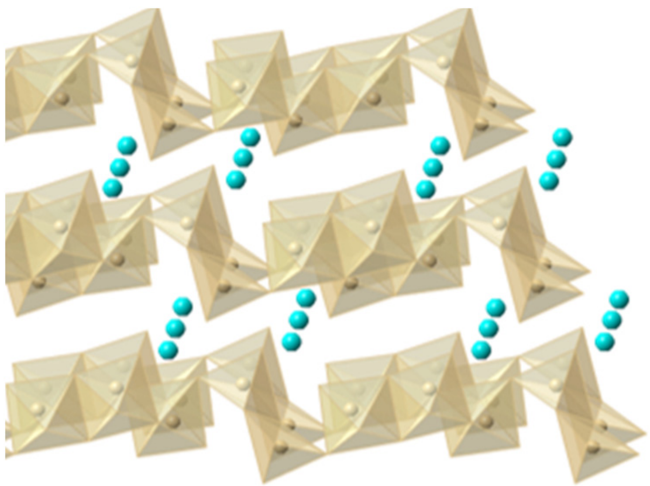
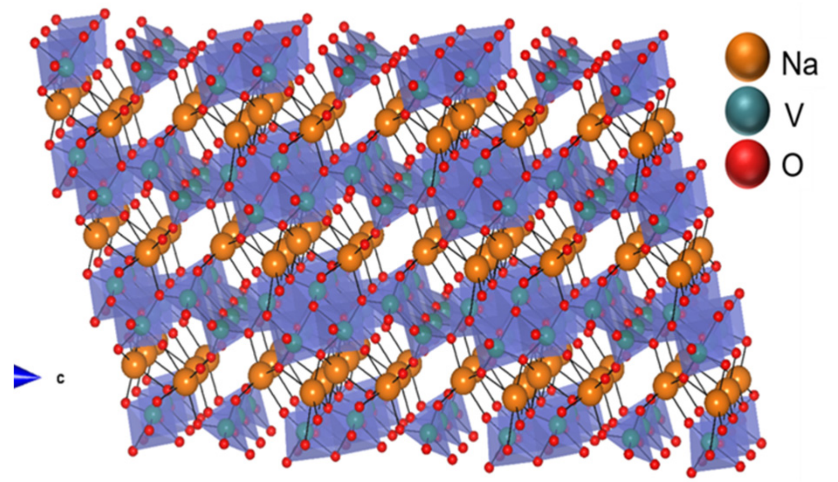
Progress Towards Scalable Electrochemical Energy Storage

Vanadium Oxide: Appealing for both nonaqueous and aqueous storage

LiV_3O_8 → NaV_3O_8

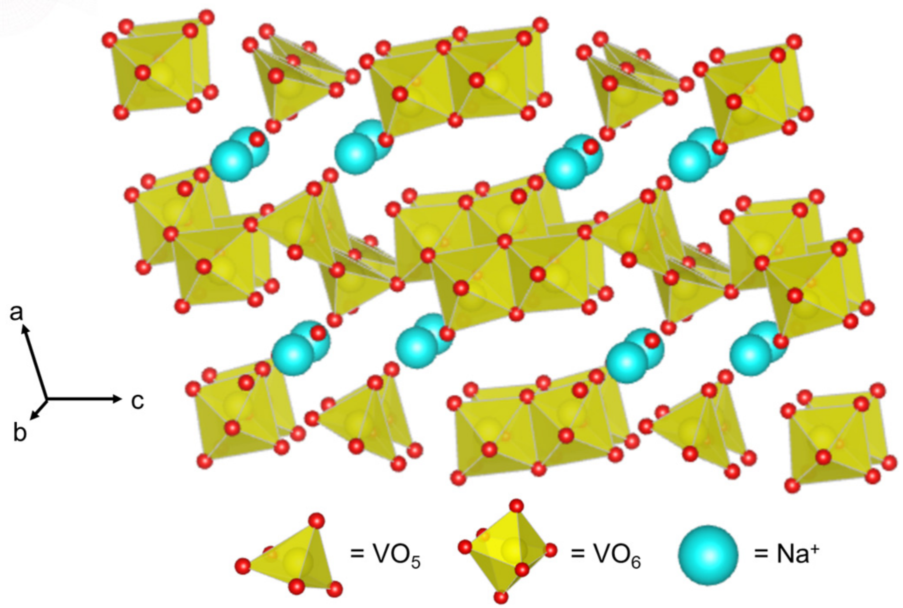




Nonaqueous Li based: Q. Zhang, A.B. Brady, C.J. Pelliccione, D.C. Bock, A.M. Bruck, J. Li, V. Sarbada, R. Hull, E.A. Stach, K.J. Takeuchi, E.S. Takeuchi, P. Liu*, A.C. Marschilok,* *Chem. Mater.,* **2017,** *29,* 2364–2373.

Aqueous Zin based: C.R. Tang†, G. Singh†, L.M. Housel†, S.J. Kim, C.D. Quilty, Y. Zhu, L. Wang, K.J. Takeuchi*, E.S. Takeuchi*, A.C. Marschilok*, *Phys. Chem. Chem. Phys.*, **2021**, *23*, 8607-8617

NaV_3O_8 for aqueous Zn storage



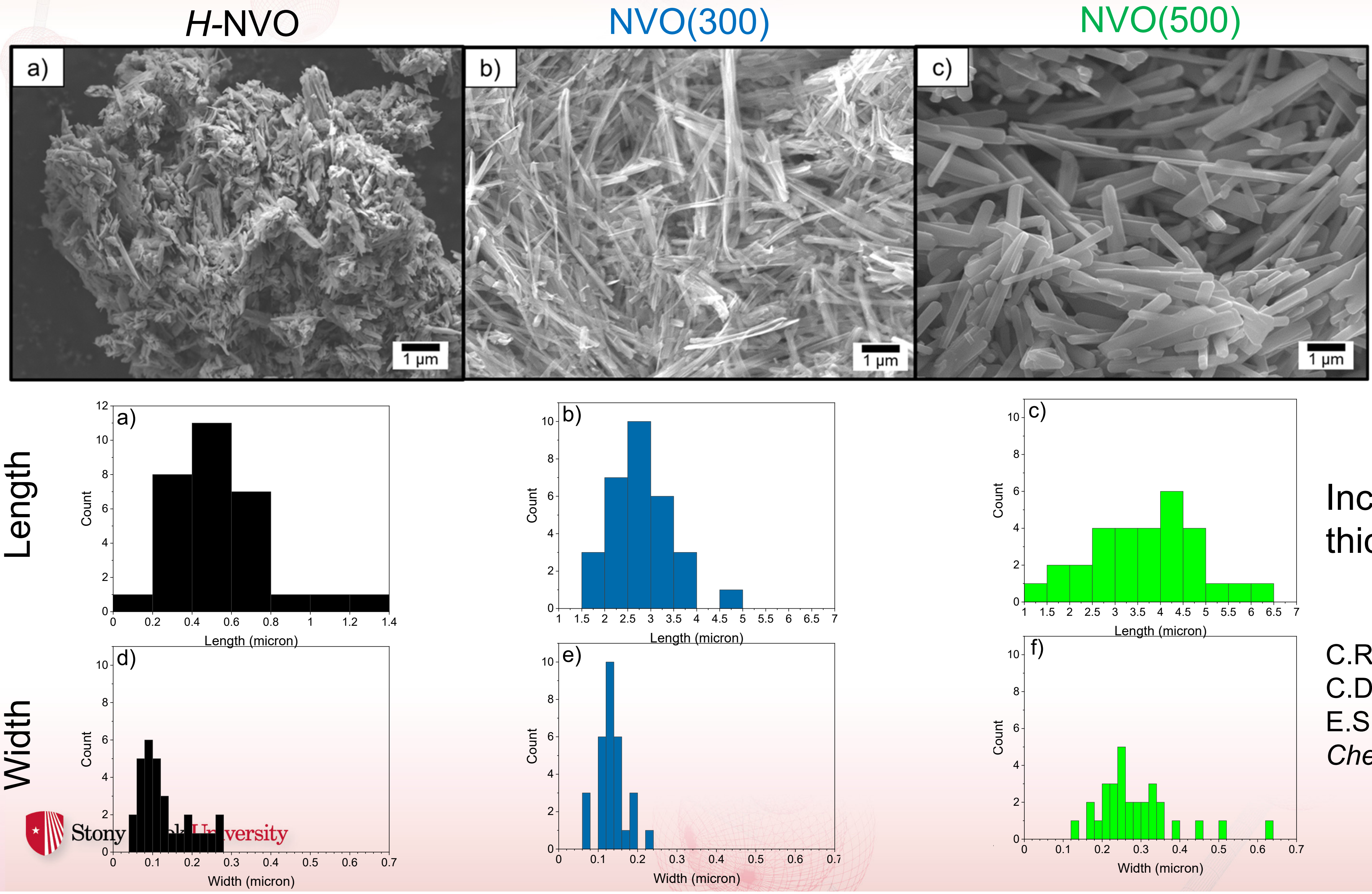
NaV_3O_8 (NVO) cathodes: **Advantages**

- High oxidation state of vanadium centers allows **multiple electron transfers.**
- **Layered structure** promotes ion intercalation.
- **Na pillar ions** provide large interlayer spacing
  - Also help **stabilize the structure**
- Extensive material tunability to control electrochemistry and charge storage mechanisms. Some tunable parameters include structural hydration, morphology, and size.

Goal: Investigate the effect of NVO material properties on Zn-ion aqueous electrochemistry

Approach: Synthetically tuned NVO material through heat treatment approach

NaV_3O_8 morphology and particle size



More uniform morphology upon annealing

H-NVO

- Belts/flakes

NVO(300)

- Thin, belt-like

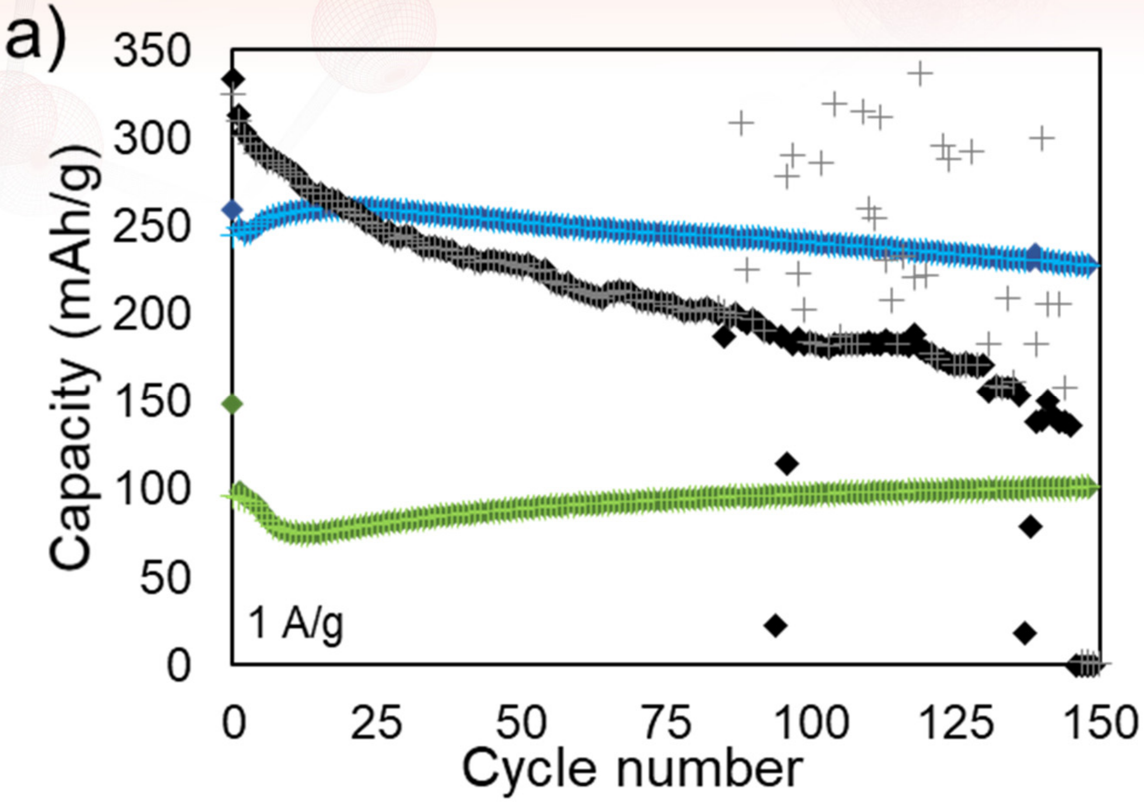
NVO(500)

- Thick, rod-like

Increased particle size and thickness consistent with XRD

C.R. Tang, G. Singh, L.M. Housel, S.J. Kim, C.D. Quilty, Y. Zhu, L. Wang, K.J. Takeuchi, E.S. Takeuchi, A.C. Marschilok, *Phys. Chem. Chem. Phys.*, **2021**, *23*, 8607-8617

NaV_3O_8 extended cycling



Galvanostatic cycling

H-NVO
- High initial capacities
- Unstable voltage profiles with increased cycling
- Catastrophic failure

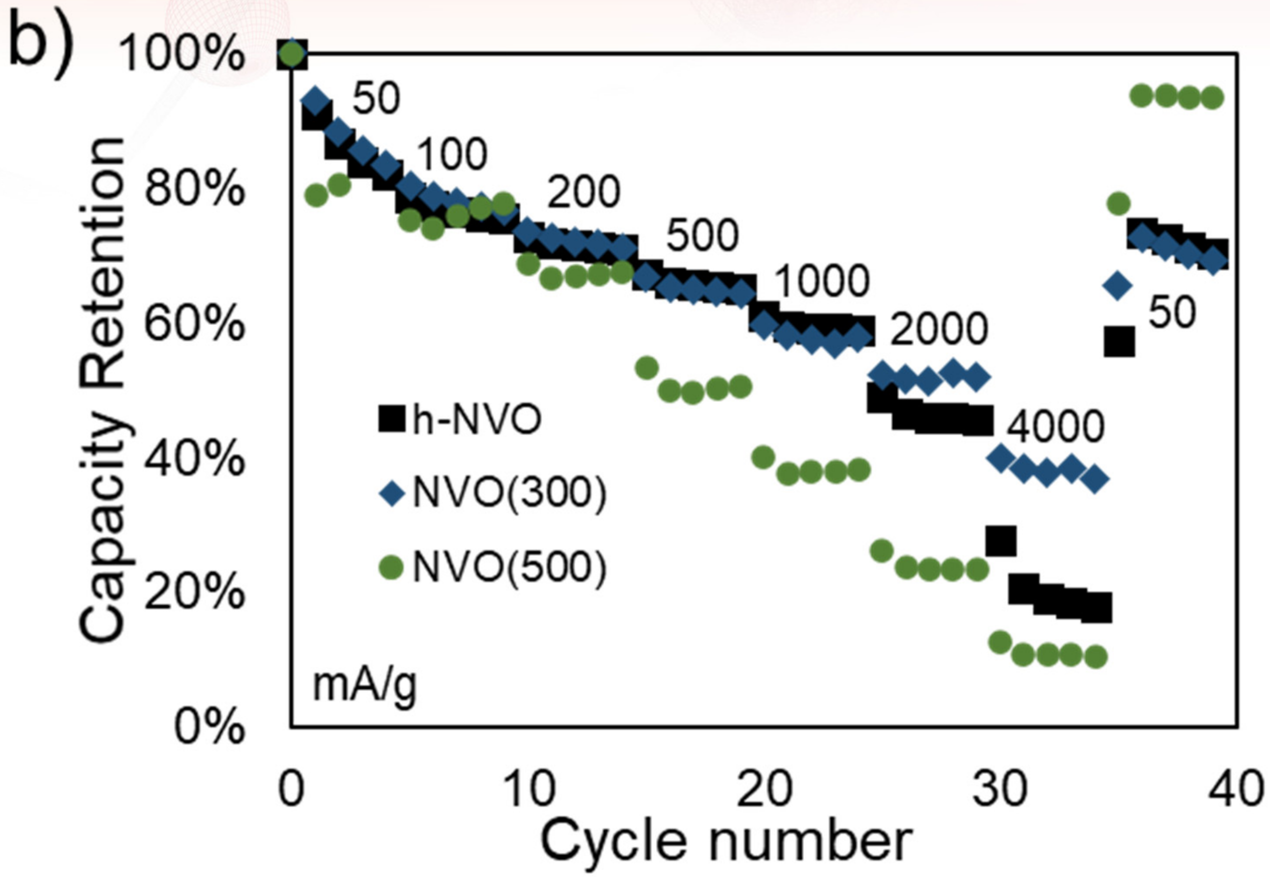
NVO(300)
- Decreased capacity but increased stability
- 10% fade after 150 cycles

NVO(500)
- Large drop in capacity after cycle 1
- Full recovery to cycle 2 capacity after 150 cycles

NVO/Zn cells
Cathode: NVO/CNT 3D porous
Anode: Zn metal
Separator: Glass fiber
Electrolyte: 2M $ZnSO_4$

C.R. Tang, G. Singh, L.M. Housel, S.J. Kim, C.D. Quilty, Y. Zhu, L. Wang, K.J. Takeuchi, E.S. Takeuchi, A.C. Marschilok, *Phys. Chem. Chem. Phys.*, **2021**, *23*, 8607-8617

NaV_3O_8 rate capability



Rate Capability
H-NVO and NVO(300) show similar capacity retention up to 4 A/g

NVO(500) shows limited rate capability, but great recovery returning to 50 mA/g

NVO/Zn cells
Cathode: NVO/CNT 3D porous
Anode: Zn metal
Separator: Glass fiber
Electrolyte: 2M $ZnSO_4$

Stony Brook University

C.R. Tang, G. Singh, L.M. Housel, S.J. Kim, C.D. Quilty, Y. Zhu, L. Wang, K.J. Takeuchi, E.S. Takeuchi, A.C. Marschilok, *Phys. Chem. Chem. Phys.*, **2021**, *23*, 8607-8617

m2m/t
molecular to mesoscale over time

NaV_3O_8 Summary

Electrochemistry

- Clear trend in electrochemical properties as morphology and water content changes with annealing
  - Tradeoff between capacity and stability
- High capacities in *h*-NVO & NVO(300) puts emphasis on effects of hydration and thickness
  - Increased ion insertion leads to greater structural change and capacity fade
- Rate capability is similar for *h*-NVO & NVO(300) at lower current densities
  - NVO(500) shows greatest capacity retention → increased particle stability
- Cyclic voltammetry revealed fastest mass transfer in NVO(300)
  - Consistent with increased degradation in *h*-NVO
  - Agrees with rate capability results

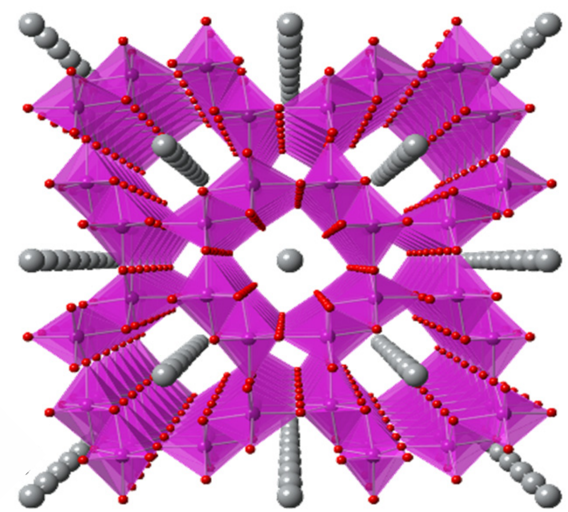
Aqueous Zinc Battery Cathode: Silver Hollandite ($Ag_2Mn_8O_{16}$)

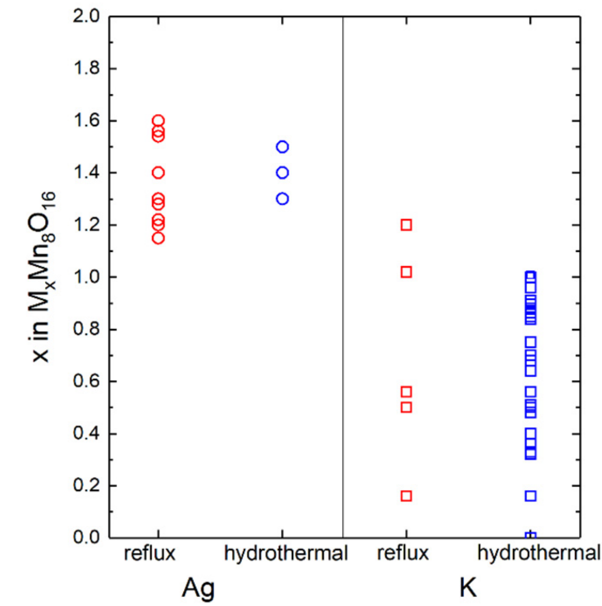
Motivation:

Aqueous Zn/MnO_2 batteries are desirable due to high abundance and safety of Zn and MnO_2

α-MnO_2 is ideal for transport studies as a synthetically tunable model 1D material

In lithium based nonaqueous batteries silver hollandite formed conductive Ag^0 upon discharge via irreversible reduction-displacement





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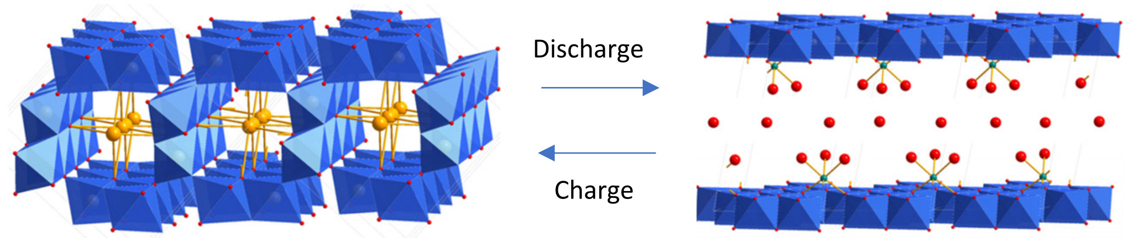
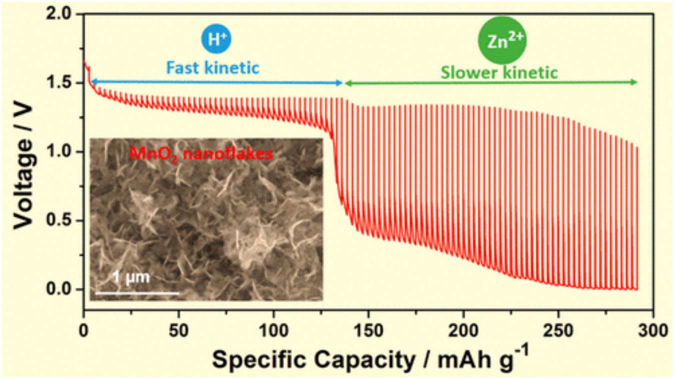
Background: Proposed Storage Mechanisms in Aqueous Zn/α-MnO_2

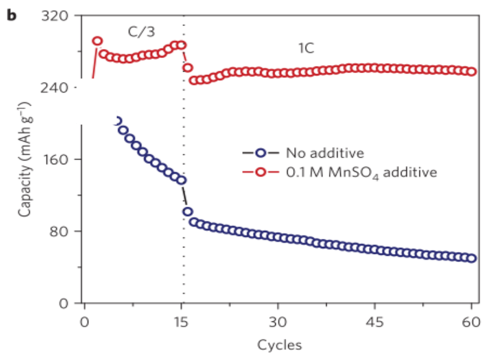
Multiple reported charge storage mechanisms

1. Zn-insertion reaction[1]
2. H^+ insertion/chemical conversion reaction[2]
3. H^+ and Zn^{2+} co-insertion/conversion[3]

Mn^{2+} dissolution plays a role and addition of Mn^{2+} additives improves capacity retention[3,4]







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By Stephanie Kossman

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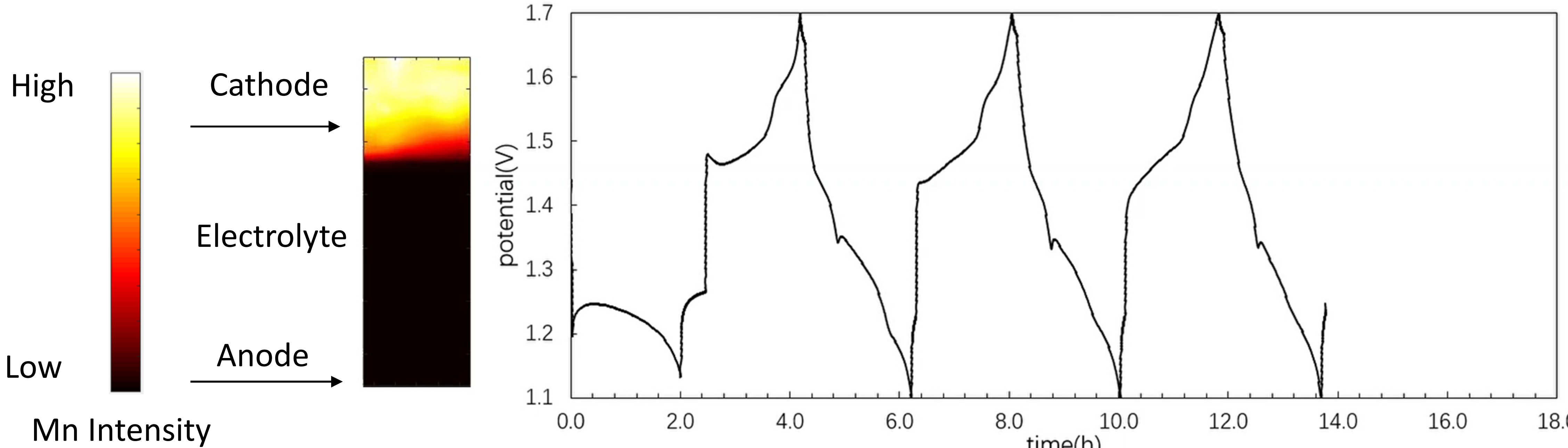
Exploring the Electrochemistry of Water-Based Batteries

Scientists identified the primary reaction mechanism in a rechargeable zinc/manganese oxide battery, paving a new path towards grid-scale energy storage

July 1, 2021

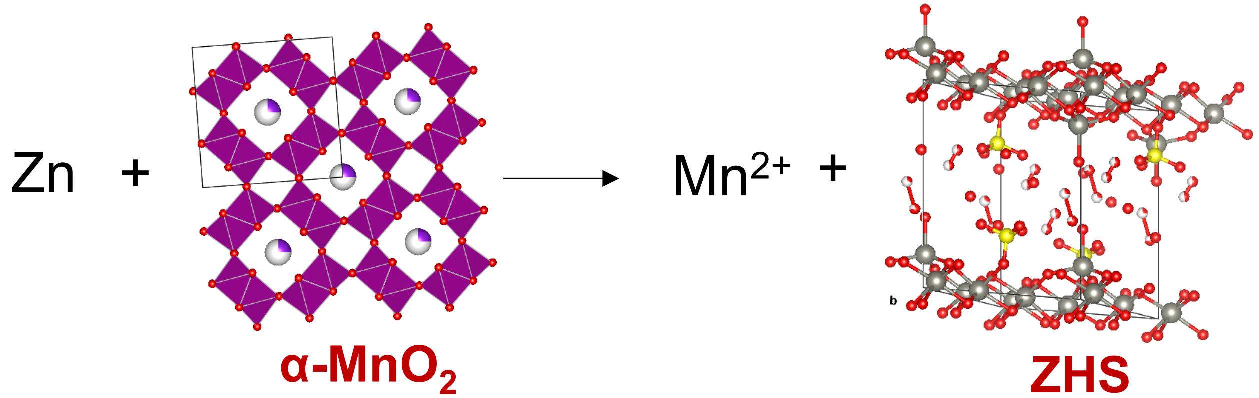
Operando Proof of Reversible Mn Dissolution-Deposition for Grid Scale Storage



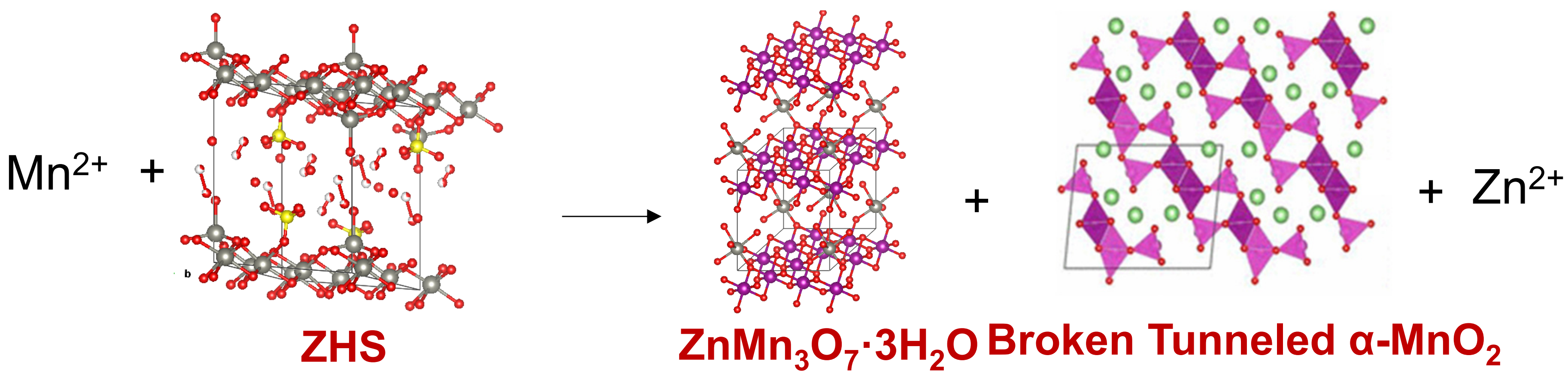
D. Wu‡, L.M. Housel‡, S-J. Kim, N. Sadique, C.D. Quilty, L. Wu, R. Tappero, S.L. Nicholas, S. Ehrlich, Y. Zhu, A.C. Marschilok, E.S. Takeuchi*, D.C. Bock*, K.J. Takeuchi*, *Energy & Environmental Science,* **2020,** 13, 4322-4333. DOI:/10.1039/D0EE02168G

The Dissolution-Deposition Zn/α-MnO_2 Mechanism

Discharge Mn^{2+} is dissolved into electrolyte, $Zn_4SO_4(OH)_6 \cdot 5H_2O_{(s)}$ (ZHS) precipitates on the surface



Charge Mn^{2+} redeposits as layered $ZnMn_3O_7 \cdot 3H_2O_{(s)}$ (Chalcophanite) or (broken) tunneled MnO_2 and ZHS dissolves.



Total Reaction

$$4Zn_{(s)} + ZnMn_3O_7 \cdot 3H_2O_{(s)} + MnO_{2(s)} + SO_{4(aq)}^{2-} + 12H_{(aq)}^{+} \rightleftharpoons Zn_4SO_4(OH)_6 \cdot 5H_2O_{(s)} + Zn_{(aq)}^{2+} + 4\,Mn_{(aq)}^{2+} + H_2O_{(l)}$$

D. Wu‡, L.M. Housel‡, S-J. Kim, N. Sadique, C.D. Quilty, L. Wu, R. Tappero, S.L. Nicholas, S. Ehrlich, Y. Zhu, A.C. Marschilok, E.S. Takeuchi*, D.C. Bock*, K.J. Takeuchi*, *Energy & Environmental Science,* **2020,** 13, 4322-4333. DOI:/10.1039/D0EE02168G

Recent Work Beyond Li-Ion Batteries

Manganese Molybdate Cathodes with Dual-redox Centers for Aqueous Zinc-ion Batteries: Impact of Electrolyte on Electrochemistry

Jason Kuang [1,2], Shan Yan [2,3], Lisa M. Housel [2,3], Steven N. Ehrlich,[4] Lu Ma,[4] Kenneth J. Takeuchi [1, 2, 3, 5], Esther S. Takeuchi [1, 2, 3, 5], Amy C. Marschilok [1, 2, 3, 5,*], Lei Wang [2,3,*]

[1]Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY, 11794, USA

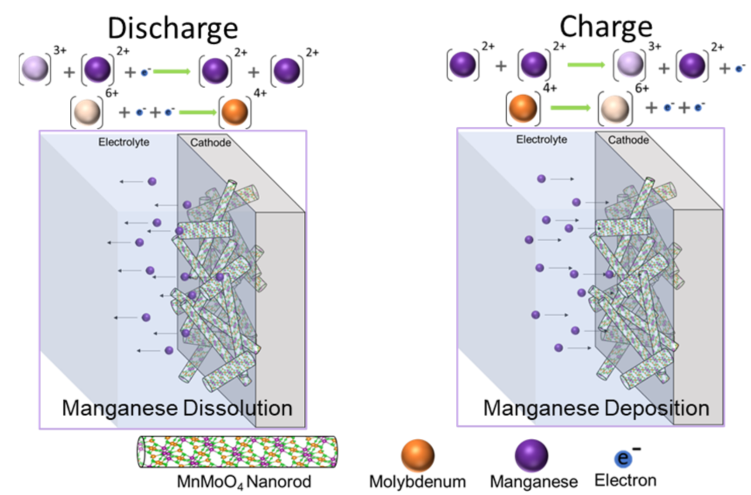
[2]Institute for Energy Sustainability and Equity, Stony Brook University, Stony Brook, NY, 11794, USA

[3]Interdisciplinary Science Department, Brookhaven National Laboratory, Upton, NY, 11973, USA

[4]National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York, 11973

[5]Department of Chemistry, Stony Brook University, Stony Brook, NY, 11794, USA

ACS Sustain. Chem. Eng., DOI 10.1021/acssuschemeng.2c04491.



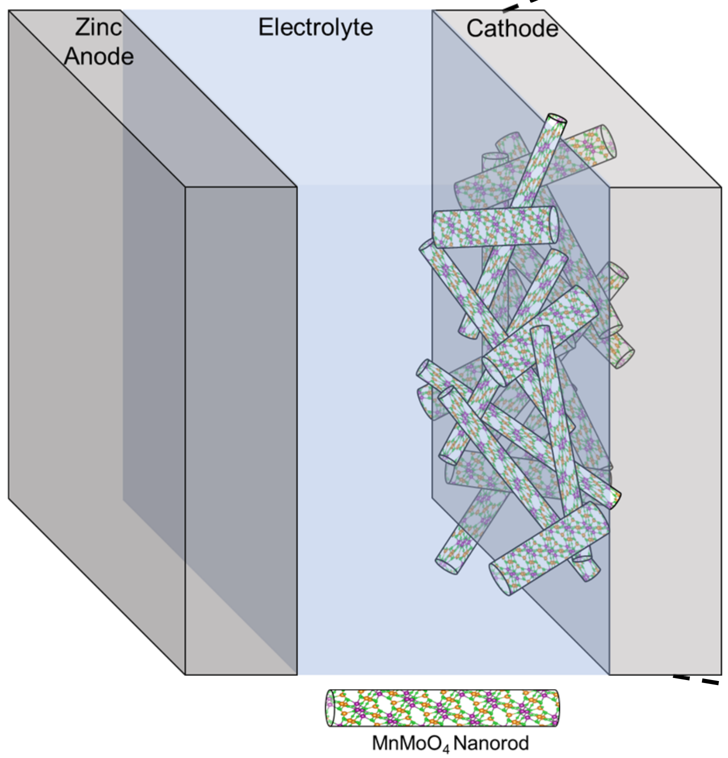
$MnMoO_4$ in Aqueous Zinc Anode Battery

Aqueous-based zinc anode battery

- Safety (nonflammable)
- Sustainable (recyclability)
- Low-cost

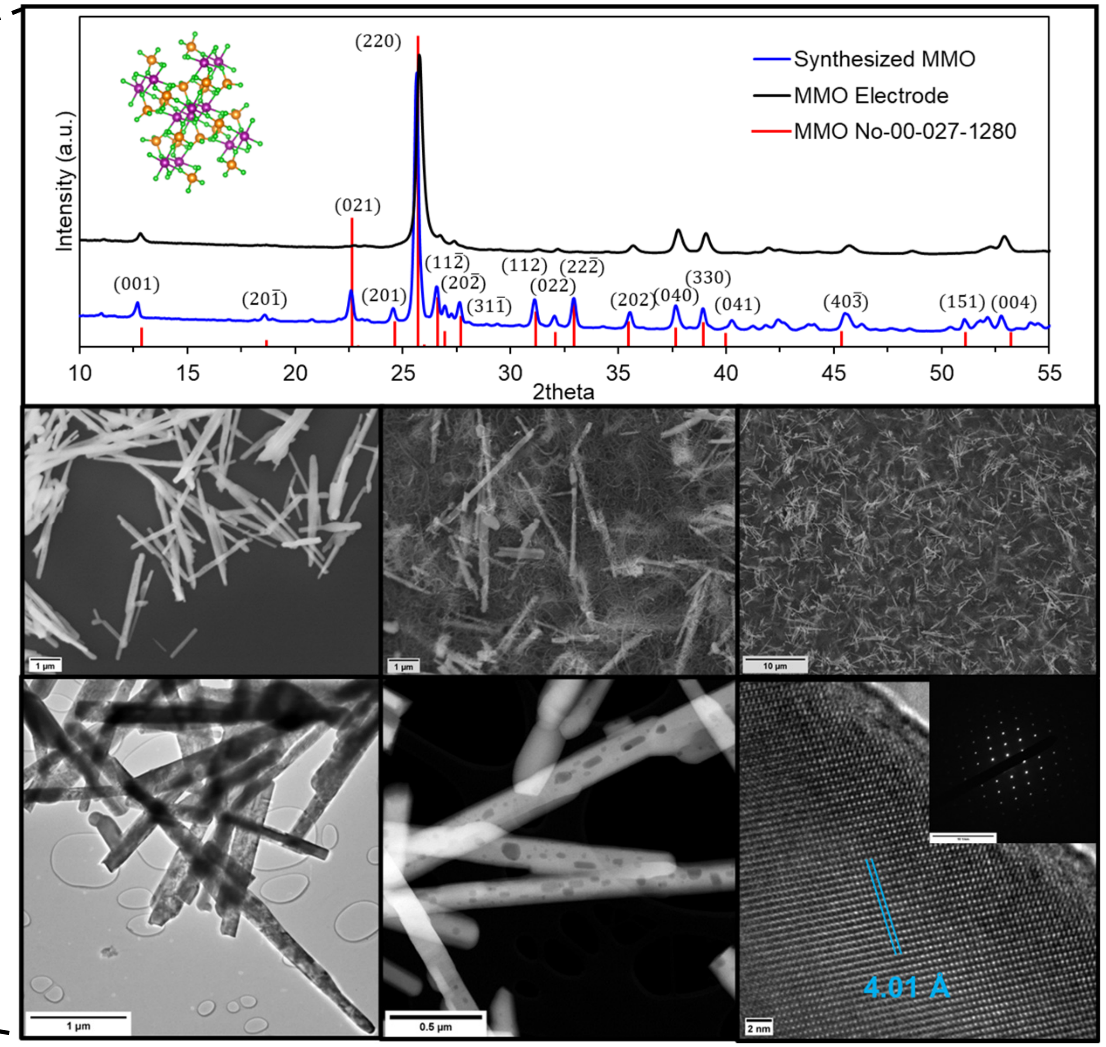
Electrolyte study

- 3 M $ZnSO_4$
- 3 M $ZnCl_2$



$MnMoO_4$ cathode

- Dual redox centers
- Sustainable
- Porous Nanorods
- Facile co-precipitation synthesis
  - Room temp.
  - Ambient atmosphere

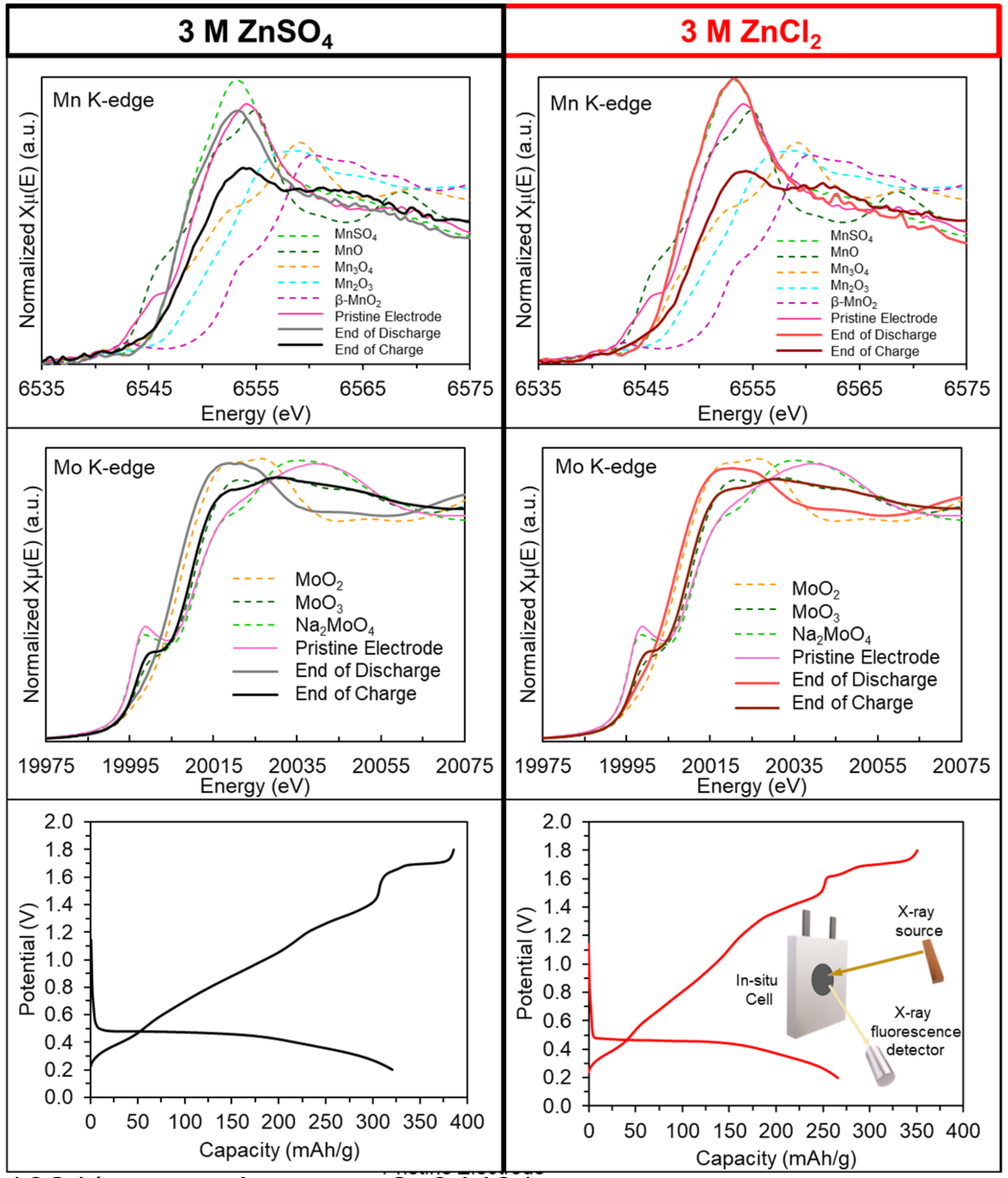


ACS Sustain. Chem. Eng., DOI 10.1021/acssuschemeng.2c04491.

Operando X-ray Absorption Spectroscopy (XAS) of the X-ray Absorption Near Edge Structure (XANES) Region Characterization

3 M $ZnSO_4$

- Mn K-edge
  - Initial: Mn^{2+}(solid)
  - End of discharge: Mn^{2+} (solution)
  - End of charge: $Mn^{2.5+}$(solid)
- Mo K-edge
  - Initial: Mo^{6+} tetrahedral site
  - End of discharge: Mo^{4+} octahedral site
  - End of charge: Mo^{6+} mixed tetrahedral and octahedral



3 M $ZnCl_2$

- Mn K-edge
  - Initial: Mn^{2+}(solid)
  - End of discharge: Mn^{2+} (solution)
  - End of charge: $Mn^{2.5+}$(solid)
- Mo K-edge
  - Initial: Mo^{6+} tetrahedral site
  - End of discharge: Mo^{4+} octahedral site
  - End of charge: Mo^{6+} mixed tetrahedral and octahedral

Data collected at beamline 7-BM, quick x-ray absorption and scattering (QAS) of the National Synchrotron Light Source II, Brookhaven National Laboratory

ACS Sustain. Chem. Eng., DOI 10.1021/acssuschemeng.2c04491.

Electrochemical Characterization: Rate Capability, Cycling at *100 and 500 mA/g*

Rate Capability

Greater capacities at higher rates observed in 3 M $ZnSO_4$

3 M $ZnSO_4$ displayed greater retention of Mo redox

3 M $ZnCl_2$ displayed greater retention of Mn redox

Cycling *100 mA/g*

Greater cycling stability and capacity observed in 3 M $ZnCl_2$

Greater retention of Mn redox observed in 3 M $ZnCl_2$

Cycling *500 mA/g*

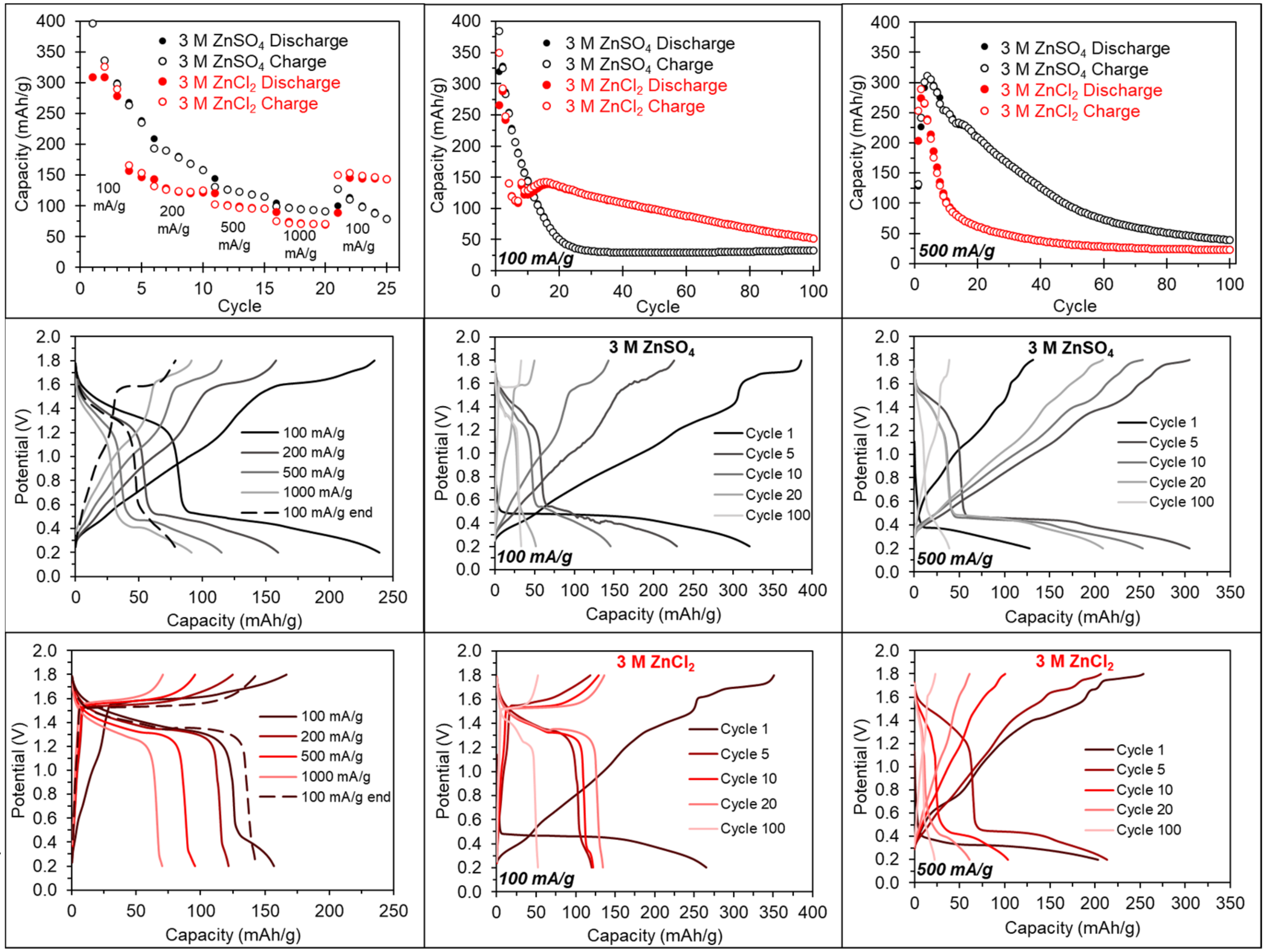
Greater cycling stability and capacity observed in 3 M $ZnSO_4$

Again, greater retention of Mo redox observed in 3 M $ZnSO_4$

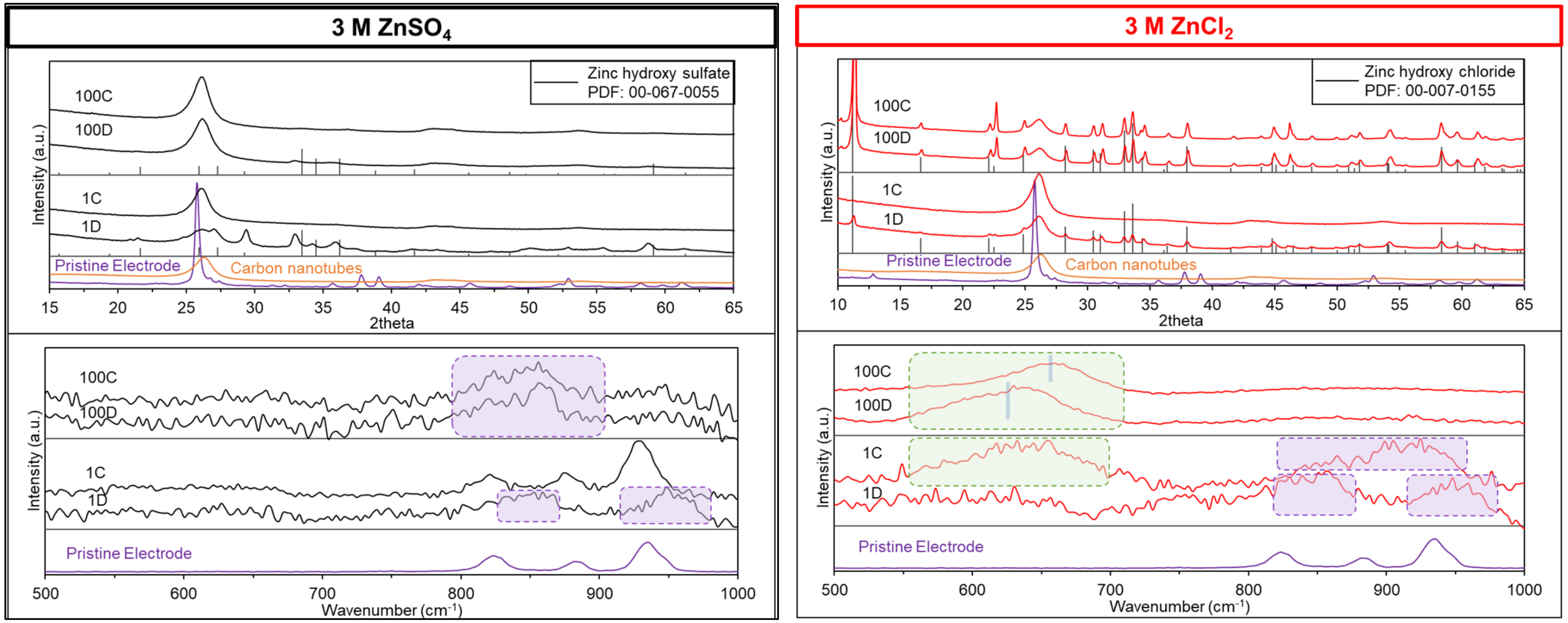
Rate dependent redox

Greater retention of the Mn redox at lower current density (*100 mA/g*)

Greater retention of the Mo redox at higher current density (*500 mA/g*)



Ex-situ Characterization of Cycled (*100 mA/g*) Cathodes in 3 M $ZnSO_4$ and $ZnCl_2$



X-ray Diffraction (XRD)

- Irreversible formation of zinc hydroxide by-products
  - $Zn_4(SO_4)(OH)_6 \cdot 3H_2O$, zinc hydroxy sulfate (ZHS)
  - $Zn_5(OH)_8Cl_2 \cdot H_2O$, zinc hydroxy chloride (ZHC)
  - Commonly observed in other aqueous zinc systems with $ZnSO_4$ and $ZnCl_2$-based electrolytes

Raman Spectroscopy

- Retention of Mo-O signal in 3 M $ZnSO_4$
- Retention of Mn-O signals in 3 M $ZnCl_2$

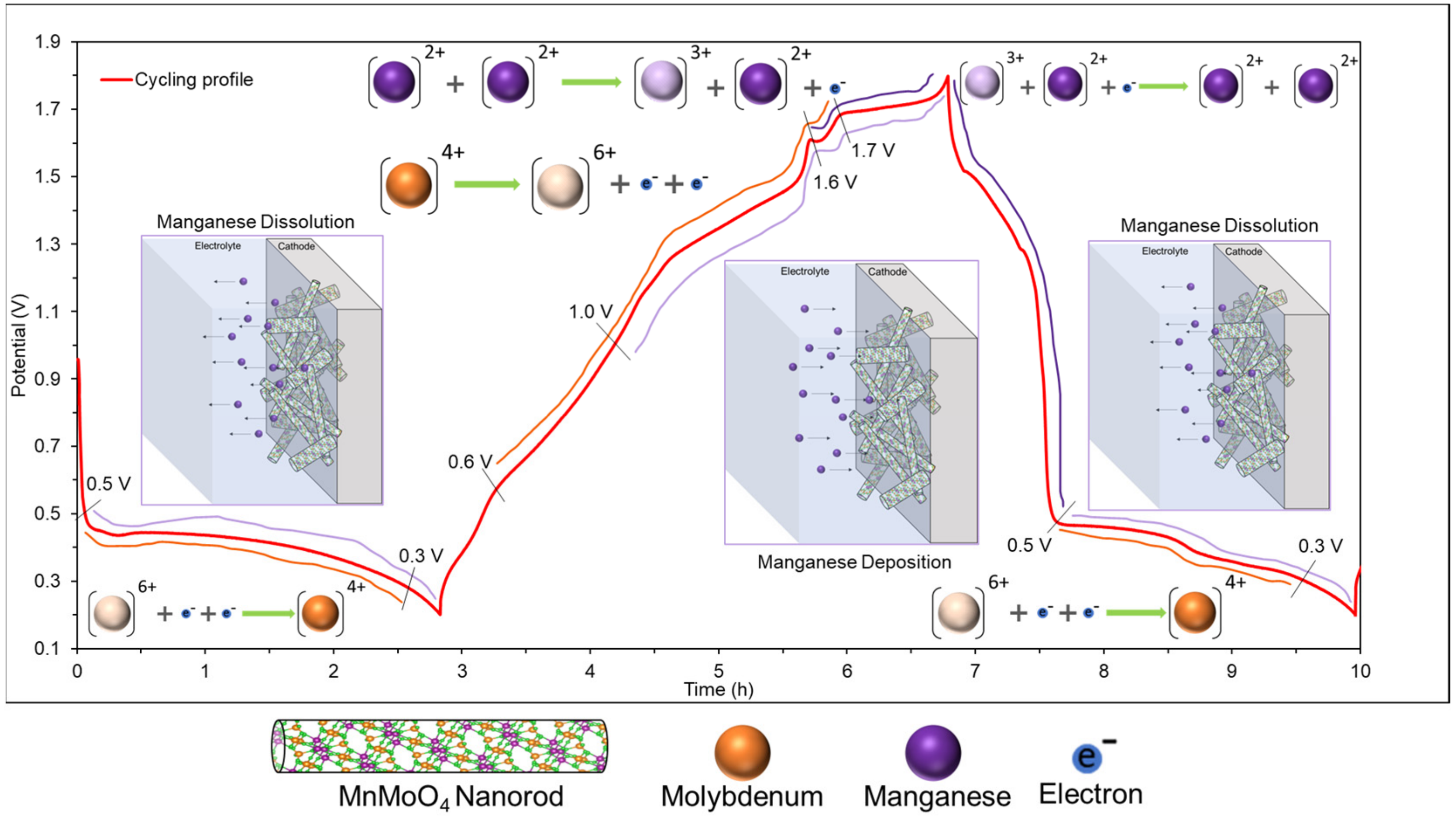
Summary Zn/$MnMoO_4$ Aqueous Battery

Dual Redox Centers
- $Mn^{2.5+}/Mn^{2+}$
- Mo^{6+}/Mo^{4+}

Anion-dependent reactions
- SO_4^{2-} : greater retention of *Mo* redox
- Cl^- : greater retention of *Mn* redox
- Electrolyte anion and dissolved active material interactions
  - Stronger interactions between Mn^{2+} (aq) and SO_4^{2-} (aq) in the electrolyte compared to Cl^- (aq).
  - Hard-Soft Acid-Base theory
  - Solubility of the salts

Rate dependance
- Higher current: higher capacity in 3 M $ZnSO_4$
  - decreased dissolution of the $MnMoO_4$
  - retained the molybdenum redox which is dependent on solid material
- Lower current: higher capacity in 3 M $ZnCl_2$
  - the dissolution of manganese is greater, which facilitated the dissolution/deposition dependent manganese redox.

Life limiting Mechanisms
- Irreversible formation of zinc hydroxide by-products
- Irreversible dissolution-deposition of the Mn redox reaction
- Parasitic Mo dissolution and deposition on the zinc anode



Conclusions

- To fully integrate renewable energy sources into the grid, an increase in energy storage systems need to be implemented
- Cost-effective GSEESS technology is still needed, since the stationary application of Li-ion batteries and redox flow technologies are costly
- Improvements in materials sourcing and cell design are required for many of the presented technologies to reduce cost for grid-scale development
- Both system stability and safety are critical factors which demand further investigation
- **To achieve a system with high safety, low cost, and long cycle life; both fundamental and applied research is required both on high and low technology readiness level GSEESSs**

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