

Mechanistic Studies of Zinc Anode Batteries

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2022 DOE OE Energy Storage Peer-Review
12Oct2022, Albuquerque, NM

Outline

- Beyond lithium ion cathode investigations
- Mechanistic study of future beyond-lithium ion systems
- Review of current status – Grid Scale Electrochemical Energy Storage Systems

Strategy

- Leverage knowledge from lithium based electrochemical investigations
- Investigate beyond-lithium ion electrode materials
- Characterize mechanistic function to gain insight regarding functional electrochemistry for beyond-lithium ion batteries
- Consider factors relevant to Grid Scale Electrochemical Energy Storage systems

Grid Scale Electrochemical Energy Storage

Beyond Li-Ion Batteries for Grid-Scale Energy Storage

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Abstract:

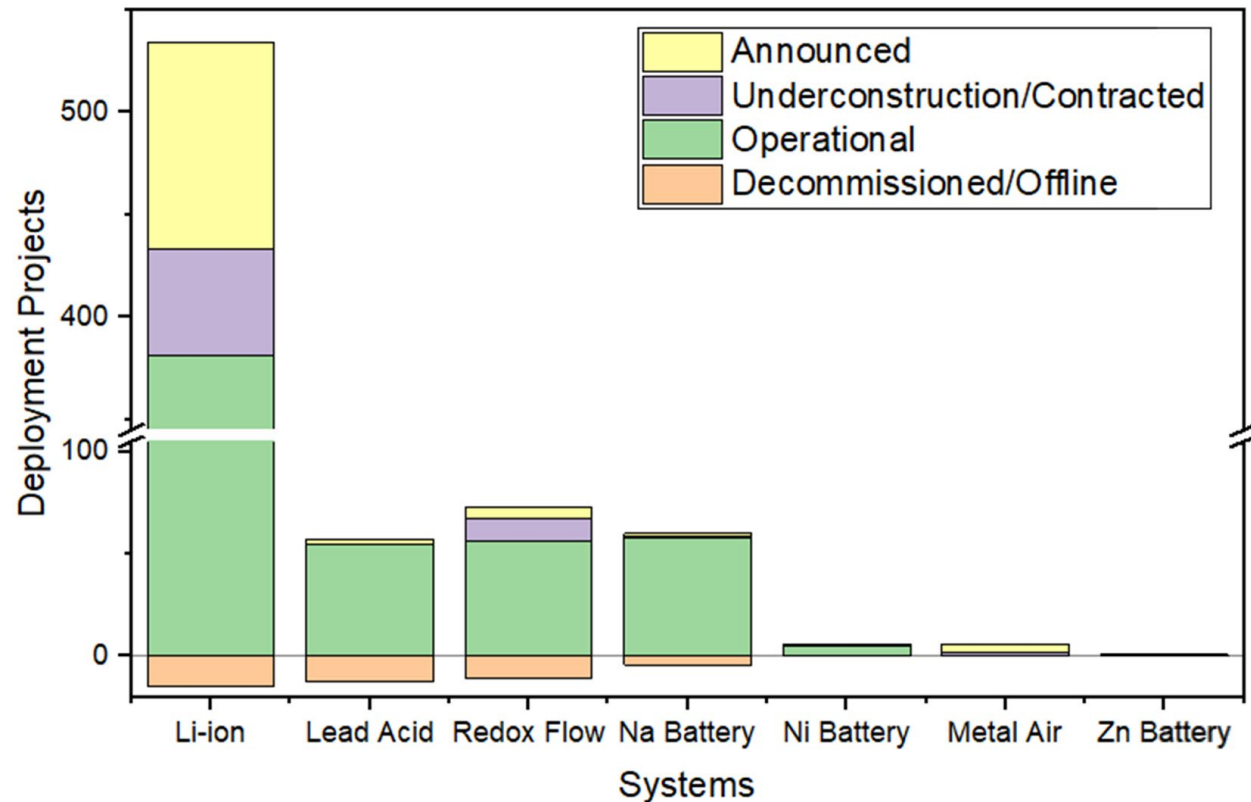
In order to improve resiliency of the grid and enable integration of renewable energy sources into the grid, the utilization of battery systems to store energy for later demand is of the utmost importance. The implementation of grid-scale electrical energy storage systems can aid in peak shaving and 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.

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4. Conclusions
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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

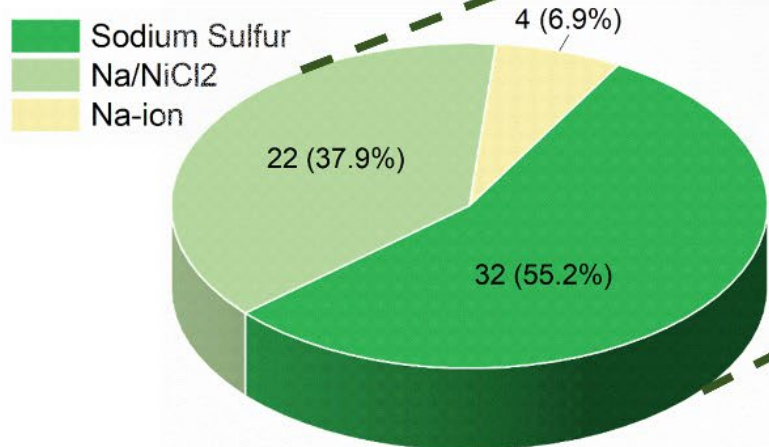
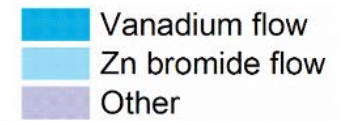
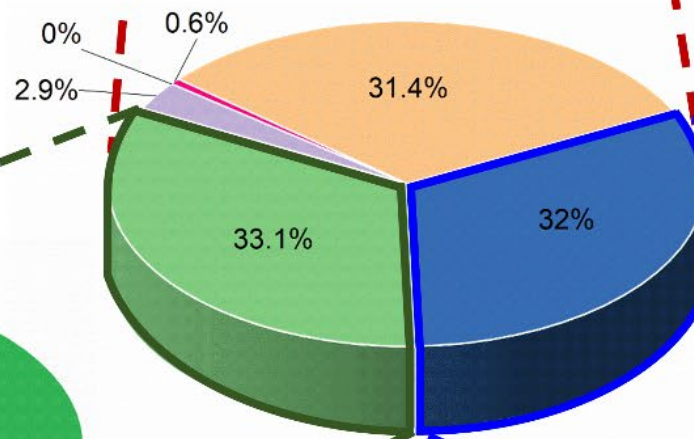
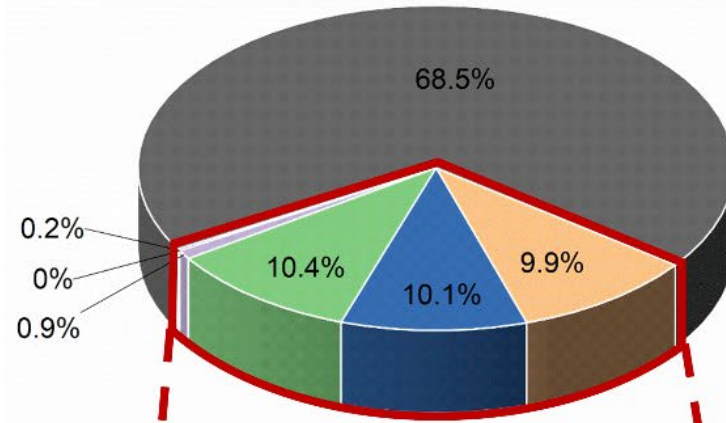


"DOE OE Global Energy Storage Database," ed: National Technology & Engineering Sciences of Sandia, 2020.

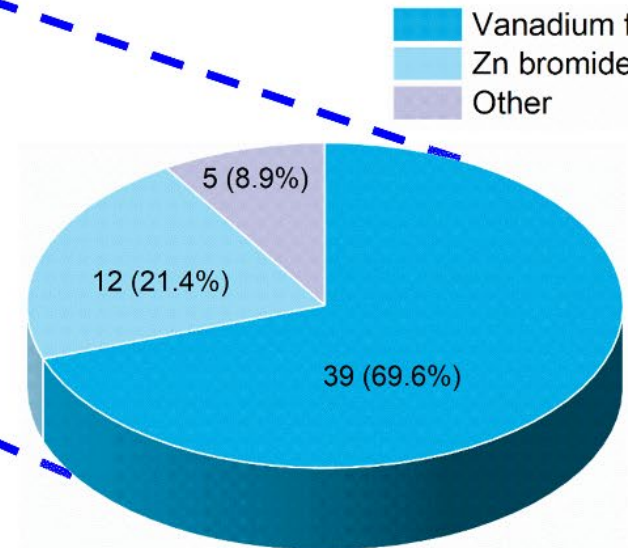
J. Hernández, I. Gyuk, C. Christensen, *2016 IEEE International Conference on Power System Technology (POWERCON)*, 2016, pp. 1-6,

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

Operational Energy Storage Systems



Sodium Battery Systems



Redox Flow Battery Systems

Operational BLI Battery Systems

Recent Work Beyond Li-Ion Batteries

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IOF Publishing

Journal of Physics D: Applied Physics

J. Phys. D: Appl. Phys. 0 (2022) xxxxxx

Roadmap

J. Phys. D: Appl. Phys. 0 (2022) xxxxxx (52pp)

<https://doi.org/10.1088/1361-6463/ac8219>

Roadmap

The 2022 applied physics by pioneering women: a roadmap

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11. Opportunities and challenges in development of multivalent batteries

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Status

Lithium-ion batteries (LIBs) are a disruptive technology that has altered the course of human society, making great progress in the last two decades, where their lightweight and high energy density have significantly impacted the portable electronics industry. There have been notable LIB contributions by women battery researchers, such as the European Battery 2030+ initiative coordinated by Edstrom (Uppsala University, Sweden). To ultimately support-grid scale energy storage worldwide, the next generation of high-performance batteries should include alternative chemistries that meet the demands for higher energy density, improved safety and reduced cost, unburdened by a constrained resource supply that limits many LIB technologies. While still emerging, multivalent systems are promising in this regard, as they can potentially lead to higher capacities than monovalent Li⁺ ions for storage of the same formula unit of working ions. Herein we discuss some recent contributions from women scientists in the specific arena of 'beyond Li-ion' multivalent battery technology. Representative examples of impactful research by women scientists in this field are shown in figure 19.

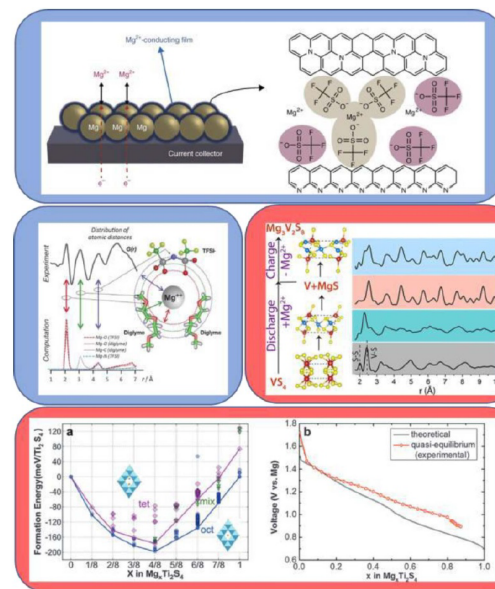


Figure 19. Electrolyte (blue) and cathode material (red) advances in development of multivalent batteries. Reproduced from [139], with permission from Springer Nature. Reproduced from [135]. CC BY 4.0. Reprinted with permission from [146]. Copyright (2018) American Chemical Society. Reproduced from [145] with permission from the Royal Society of Chemistry.

A C M acknowledges support from the US Department of Energy, Office of Electricity, administered through Sandia National Laboratories, Purchase Order #1955692. C B acknowledges support from Paul M Rady Mechanical Engineering and College of Engineering and Applied Science at University of Colorado Boulder.

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,*}

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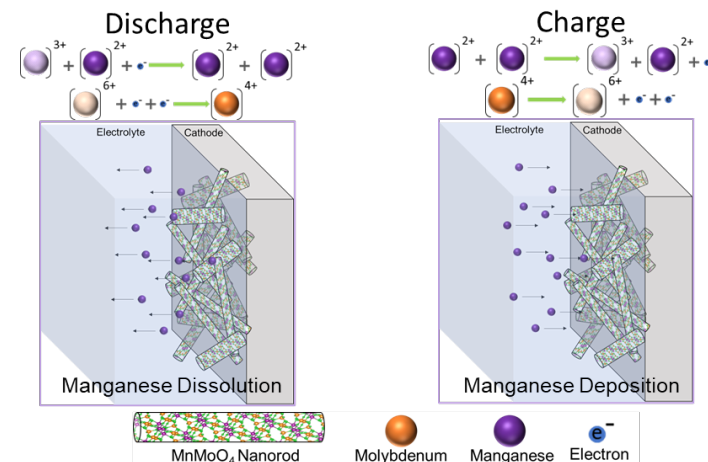
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Under revision, *ACS Sustain. Chem. Eng.*



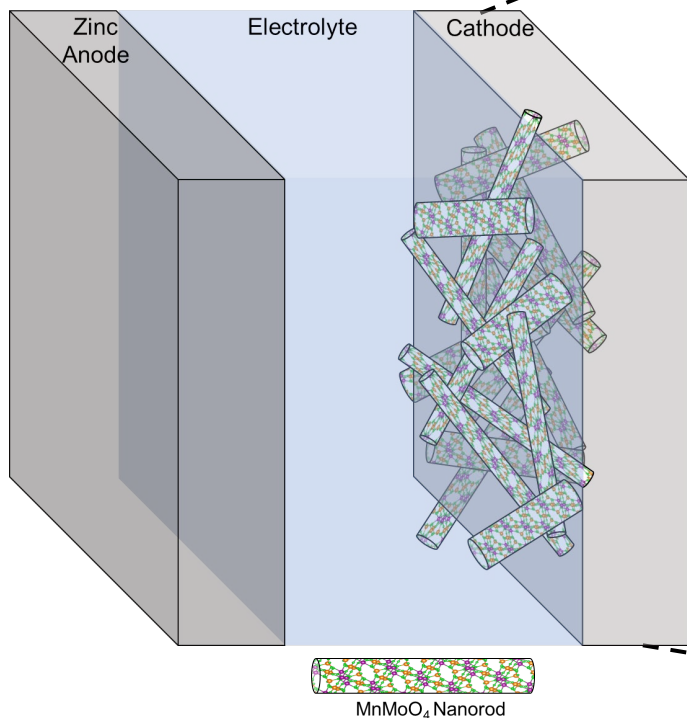
MnMoO₄ in Aqueous Zinc Anode Battery

Aqueous-based zinc anode battery

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

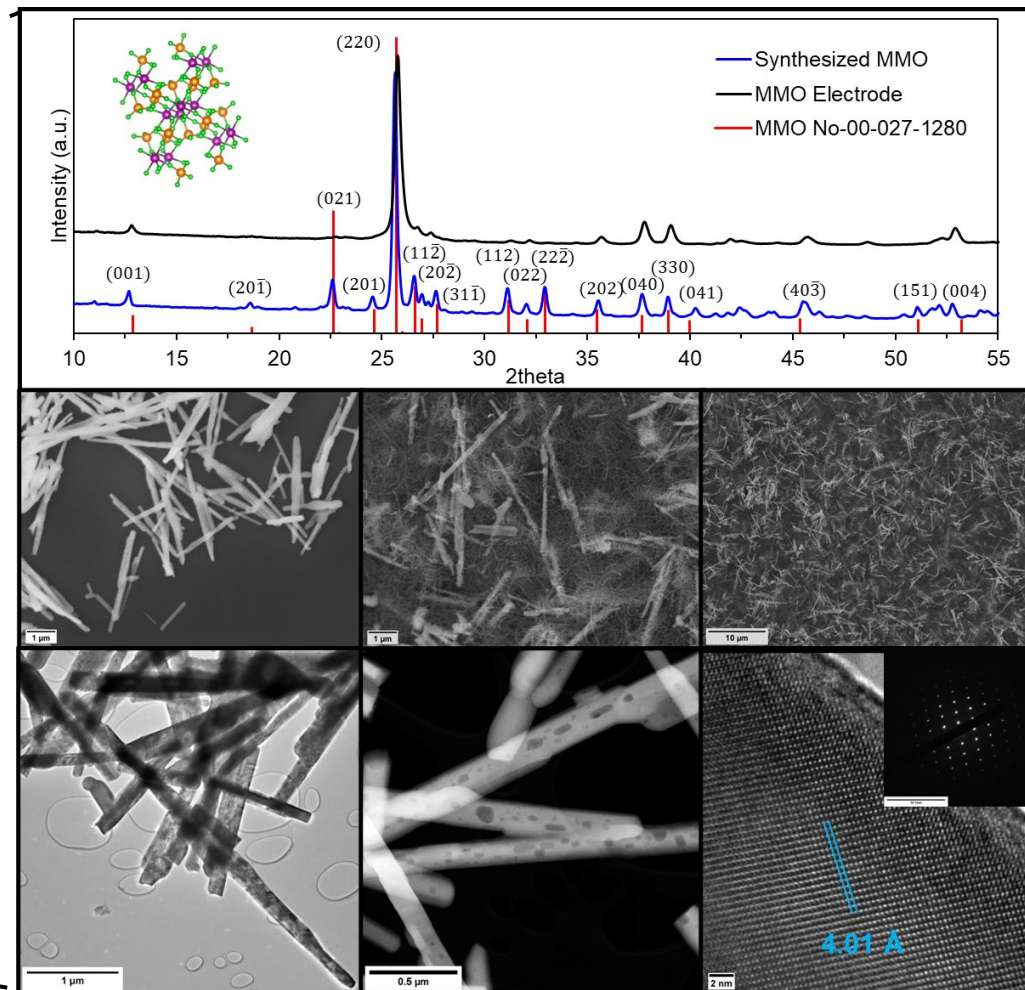
Electrolyte study

- 3 M ZnSO₄
- 3 M ZnCl₂



MnMoO₄ cathode

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



Electrochemical Characterization: Cyclic Voltammetry

Multiple cycles at 0.1 mV/s

- Initially had multiple redox peaks
- Subsequent cycles
 - redox peaks below 1.0 V reduced in current density and the cathodic peak resolved into two separate peaks at 0.30 and 0.40 V
 - continue to reduce until no longer present
 - Irreversible redox reactions

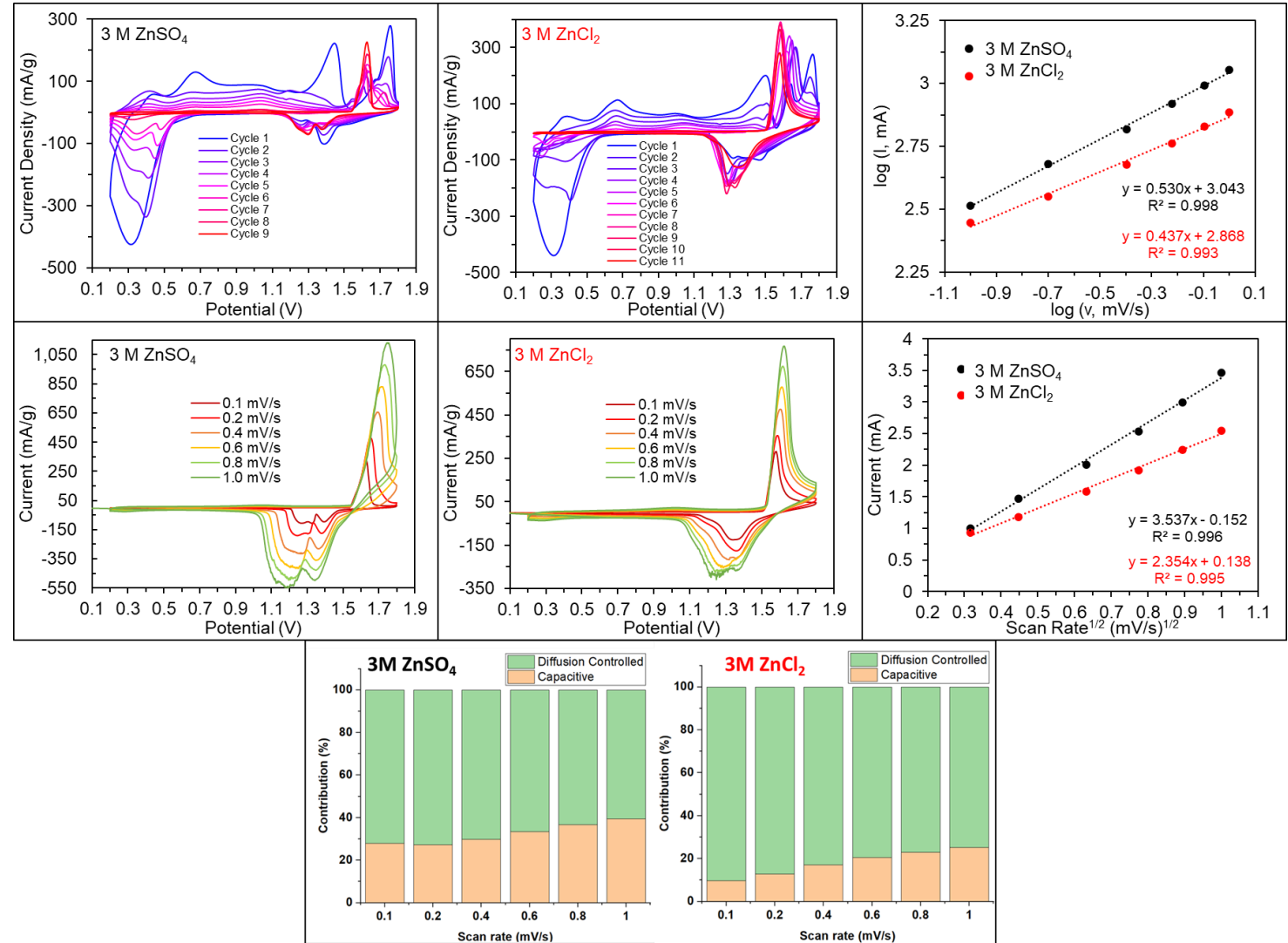
Varied scan rates (0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mV/s)

Log(scan rate) vs. Log(current)

- Diffusion-controlled process
 - More so in 3 M ZnCl₂
- Increase in capacitance with increased scan rates

Randles-Sevcik (scan rate^{1/2} vs. current)

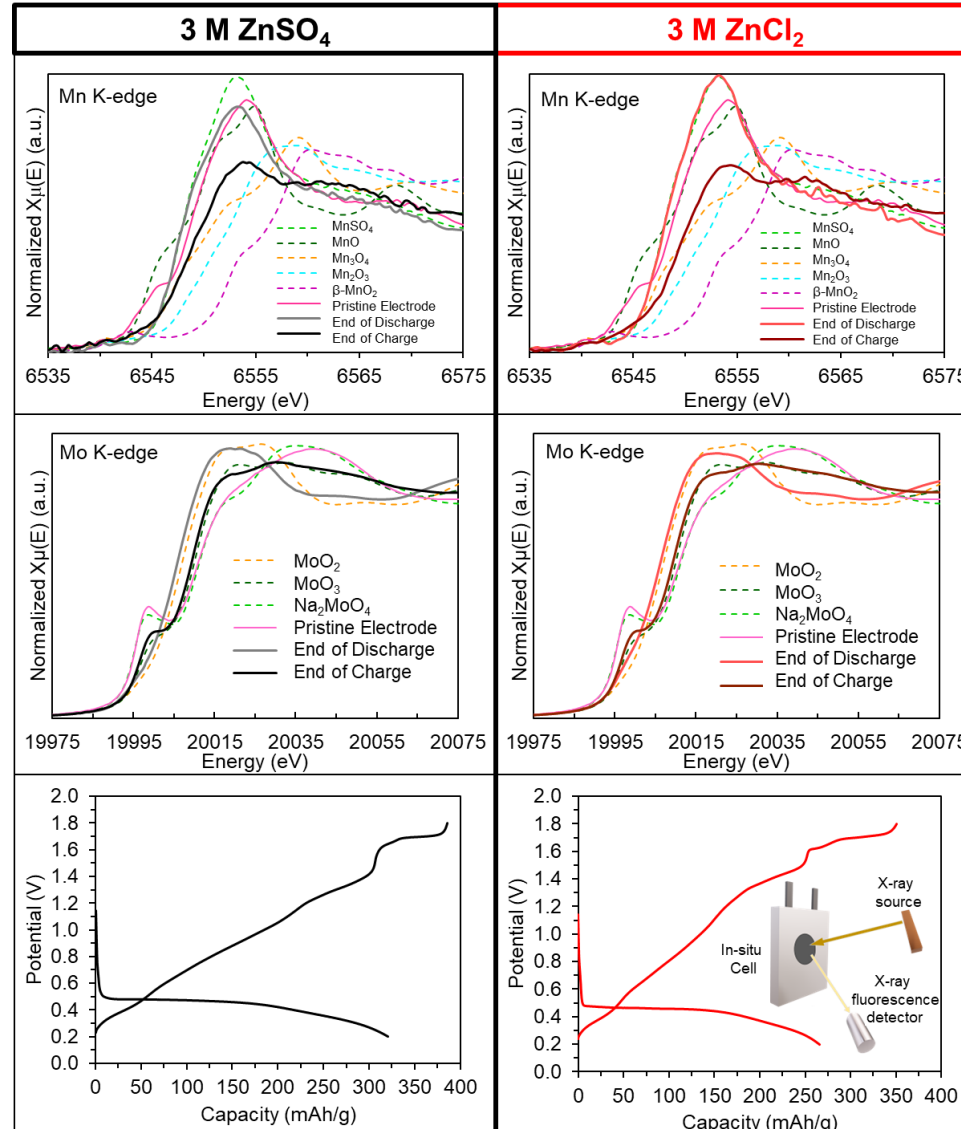
- 3 M ZnSO₄ has greater diffusion coefficient



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

3 M ZnSO₄

- Mn K-edge
 - Initial: Mn²⁺(solid)
 - End of discharge: Mn²⁺(solution)
 - End of charge: Mn^{2.5+}(solid)
- Mo K-edge
 - Initial: Mo⁶⁺ tetrahedral site
 - End of discharge: Mo⁴⁺ octahedral site
 - End of charge: Mo⁶⁺ mixed tetrahedral and octahedral

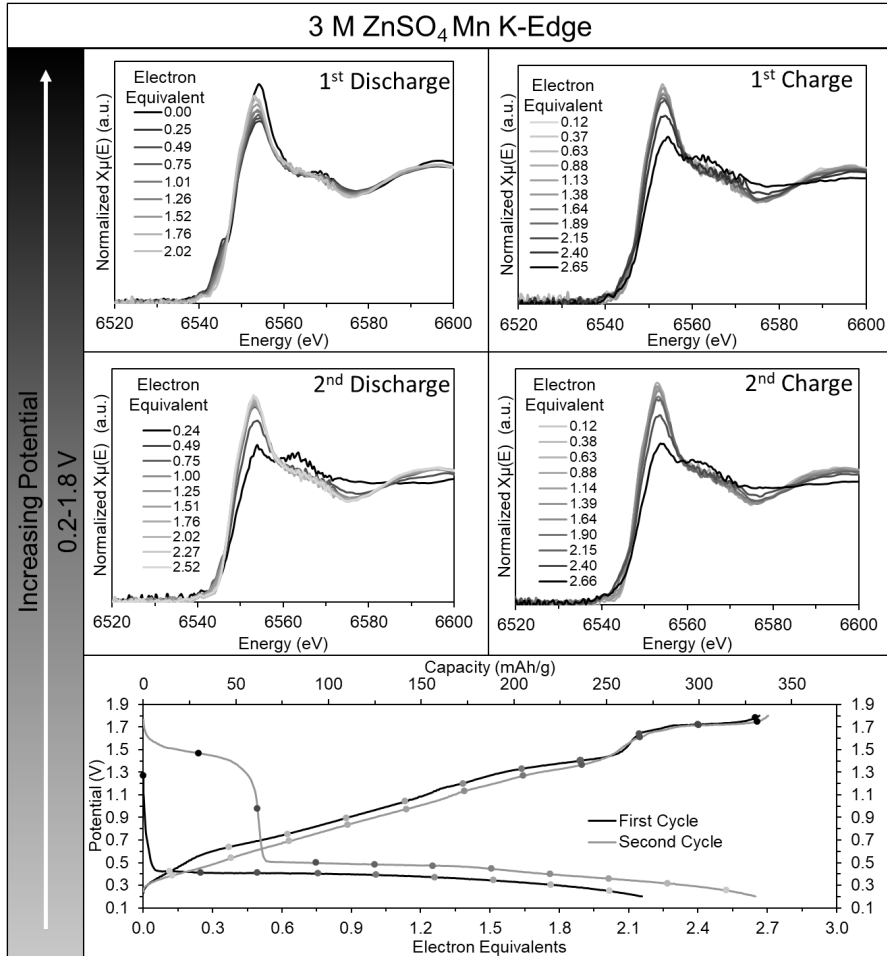


3 M ZnCl₂

- Mn K-edge
 - Initial: Mn²⁺(solid)
 - End of discharge: Mn²⁺(solution)
 - End of charge: Mn^{2.5+}(solid)
- Mo K-edge
 - Initial: Mo⁶⁺ tetrahedral site
 - End of discharge: Mo⁴⁺ octahedral site
 - End of charge: Mo⁶⁺ 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

Operando XAS of the XANES Region Characterization: 3 M ZnSO₄

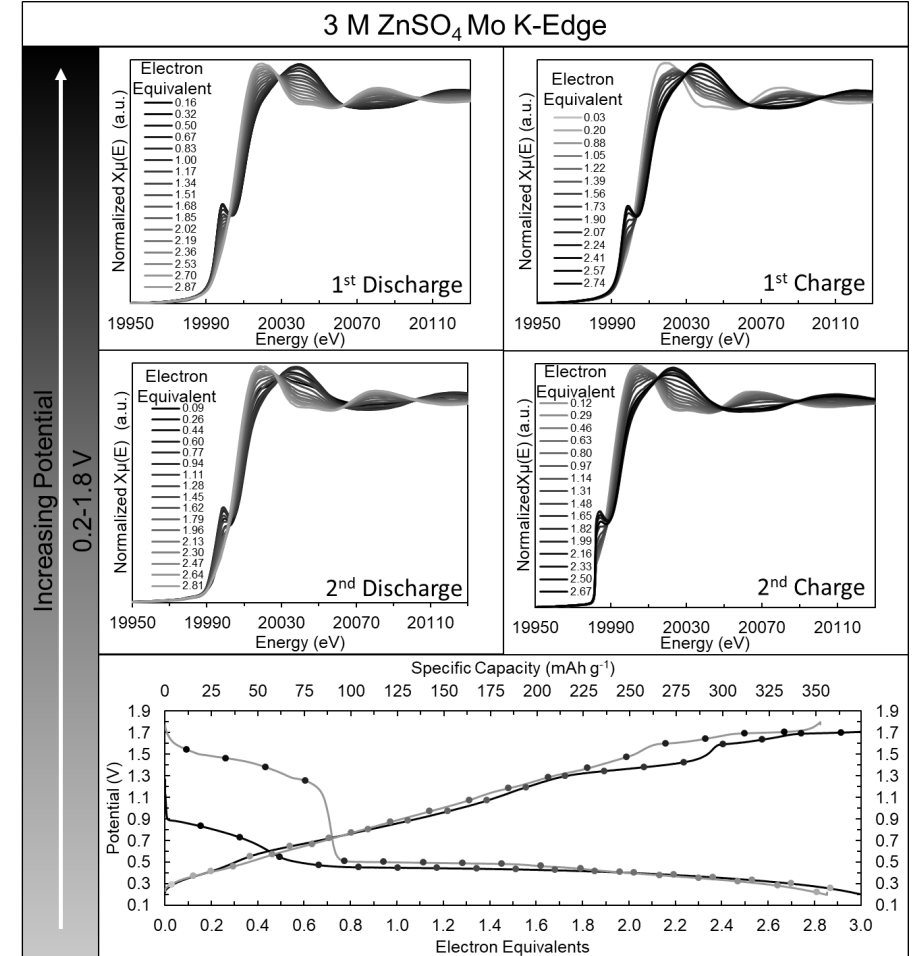


Manganese

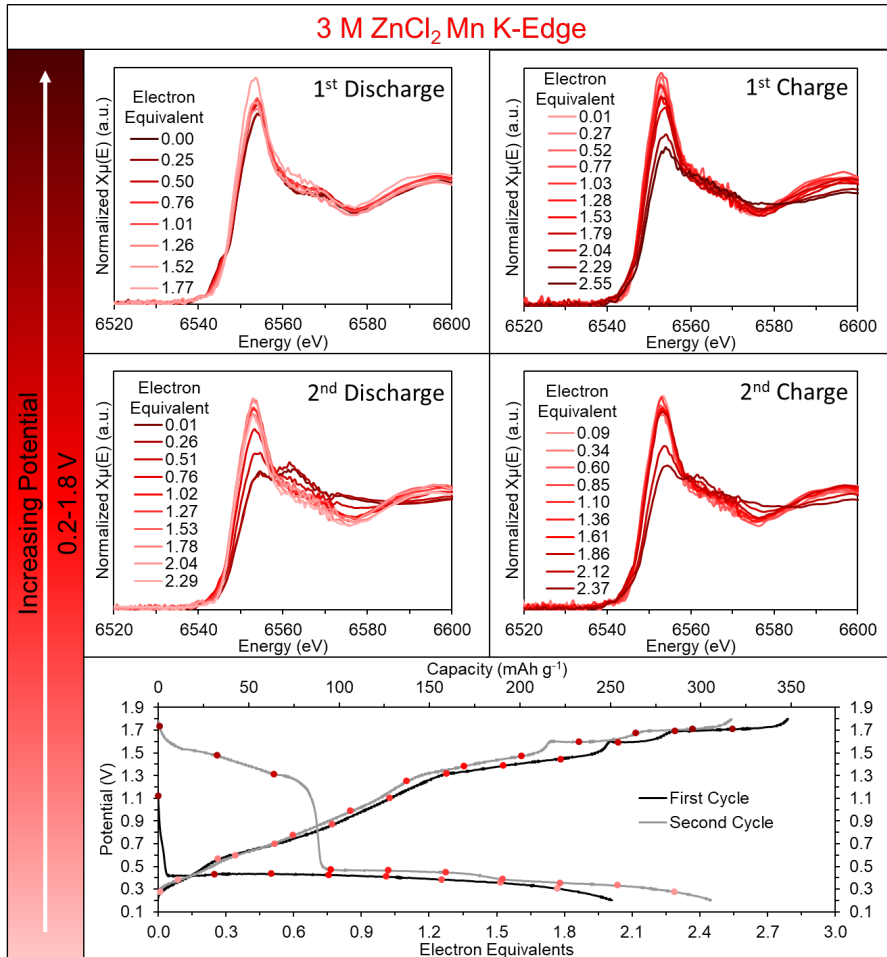
- First discharge:
 - gradual change from solid to solution Mn²⁺ (OCP to 0.2 V)
- First charge:
 - Mn²⁺ in solution to Mn²⁺ in solid at (0.2 to 1.0 V)
 - Mn²⁺ to Mn^{2.5+} in solid (1.6 to 1.8 V)
- Second discharge:
 - Mn^{2.5+} to Mn²⁺ in solid (1.8 to 0.5 V)
 - Mn²⁺ to Mn²⁺ in solution (0.5 to 0.2 V)
- Second Charge:
 - Mn²⁺ in solution to Mn²⁺ in solid at (0.2 to 1.0 V)
 - Mn²⁺ to Mn^{2.5+} in solid (1.6 to 1.8 V)

Molybdenum

- First discharge:
 - Mo⁶⁺ to Mo⁴⁺ (OCP to 0.4 V)
- First charge:
 - Mo⁴⁺ to Mo⁶⁺ tetrahedral (0.6 to 1.64 V)
 - Mo⁶⁺ tetrahedral to Mo⁶⁺ mixed tetrahedral and octahedral (1.64 to 1.8 V)
- Second discharge:
 - Mo⁶⁺ mixed tetrahedral and octahedral to Mo⁶⁺ tetrahedral (1.8 to 0.5 V)
 - Mo⁶⁺ to Mo⁴⁺ (0.5 to 0.2 V)
- Second charge:
 - Mo⁴⁺ to Mo⁶⁺ tetrahedral (0.2 to 1.64 V)
 - Mo⁶⁺ tetrahedral to Mo⁶⁺ mixed tetrahedral and octahedral (1.64 to 1.8 V)



Operando XAS of the XANES Region Characterization: 3 M ZnCl₂



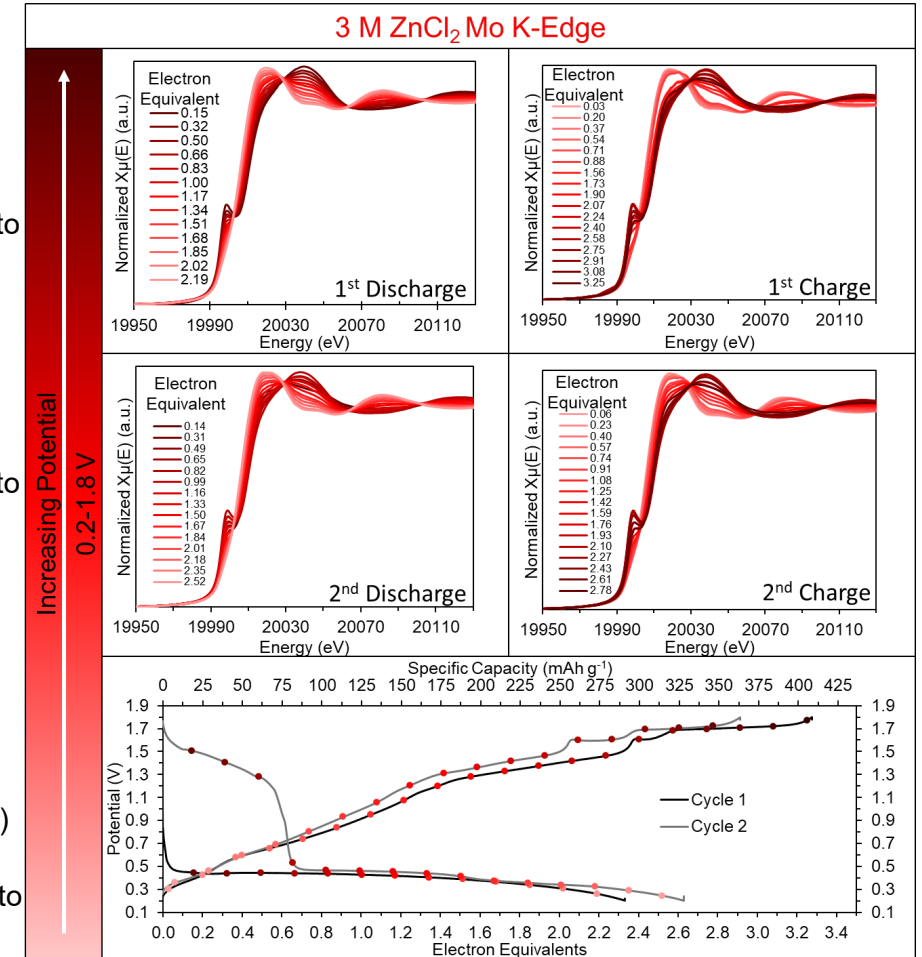
Similar results to 3 M ZnSO₄

Manganese

- First discharge:
 - Mn²⁺ to Mn²⁺ in solution (OCP to 0.2 V)
- First charge:
 - Mn²⁺ in solution to Mn²⁺ in solid at (0.2 to 1.0 V)
 - Mn²⁺ to Mn^{2.5+} (1.6 to 1.8 V)
- Second discharge:
 - Mn^{2.5+} to Mn²⁺ (1.8 to 0.5 V)
 - Mn²⁺ to Mn²⁺ in solution (0.5 to 0.2 V)
- Second Charge:
 - Mn²⁺ in solution to Mn²⁺ in solid at (0.2 to 1.0 V)
 - Mn²⁺ to Mn^{2.5+} (1.6 to 1.8 V)

Molybdenum

- First discharge:
 - Mo⁶⁺ to Mo⁴⁺ (OCP to 0.4 V)
- First charge:
 - Mo⁴⁺ to Mo⁶⁺ tetrahedral (0.6 to 1.7 V)
 - Mo⁶⁺ tetrahedral to Mo⁶⁺ mixed tetrahedral and octahedral (1.7 to 1.8 V)
- Second discharge:
 - Mo⁶⁺ mixed tetrahedral and octahedral to Mo⁶⁺ tetrahedral (1.8 to 0.5 V)
 - Mo⁶⁺ to Mo⁴⁺ (0.5 to 0.2 V)
- Second charge:
 - Mo⁴⁺ to Mo⁶⁺ tetrahedral (0.6 to 1.7 V)
 - Mo⁶⁺ tetrahedral to Mo⁶⁺ mixed tetrahedral and octahedral (1.7 to 1.8 V)



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

Rate Capability

Greater capacities at higher rates observed in 3 M ZnSO₄

3 M ZnSO₄ displayed greater retention of Mo redox

3 M ZnCl₂ displayed greater retention of Mn redox

Cycling 100 mA/g

Greater cycling stability and capacity observed in 3 M ZnCl₂

Greater retention of Mn redox observed in 3 M ZnCl₂

Cycling 500 mA/g

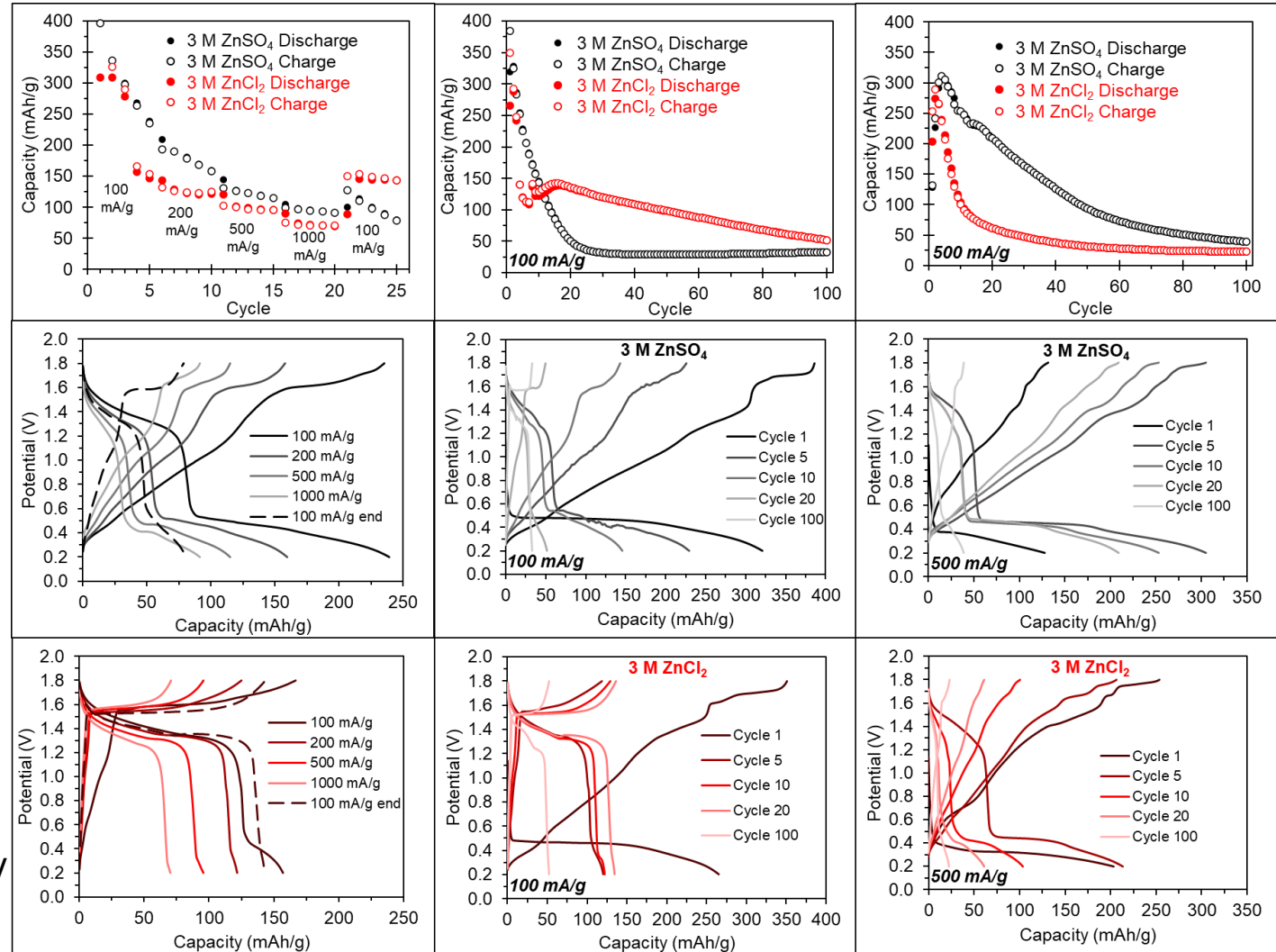
Greater cycling stability and capacity observed in 3 M ZnSO₄

Again, greater retention of Mo redox observed in 3 M ZnSO₄

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)



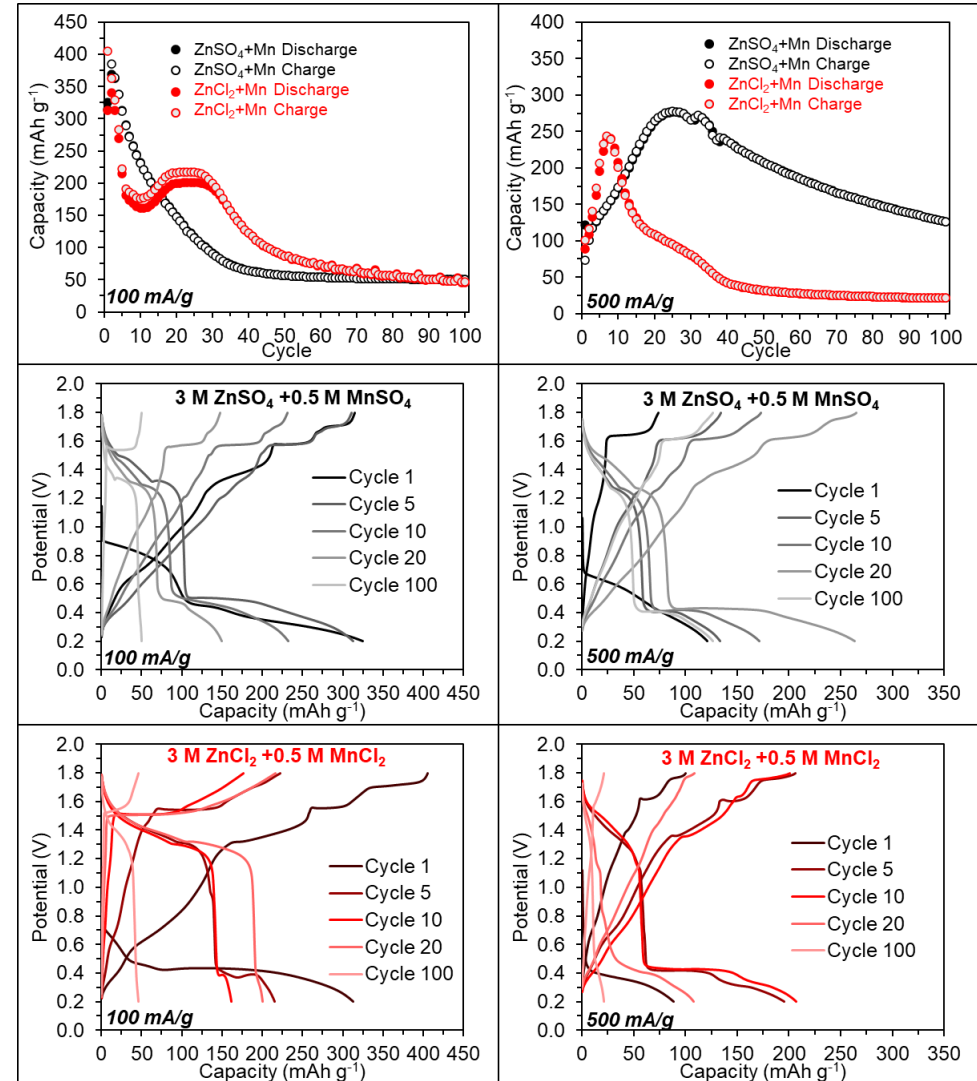
Manganese additive - Electrochemical Characterization: Cycling at 100 and 500 mA/g

Manganese additive

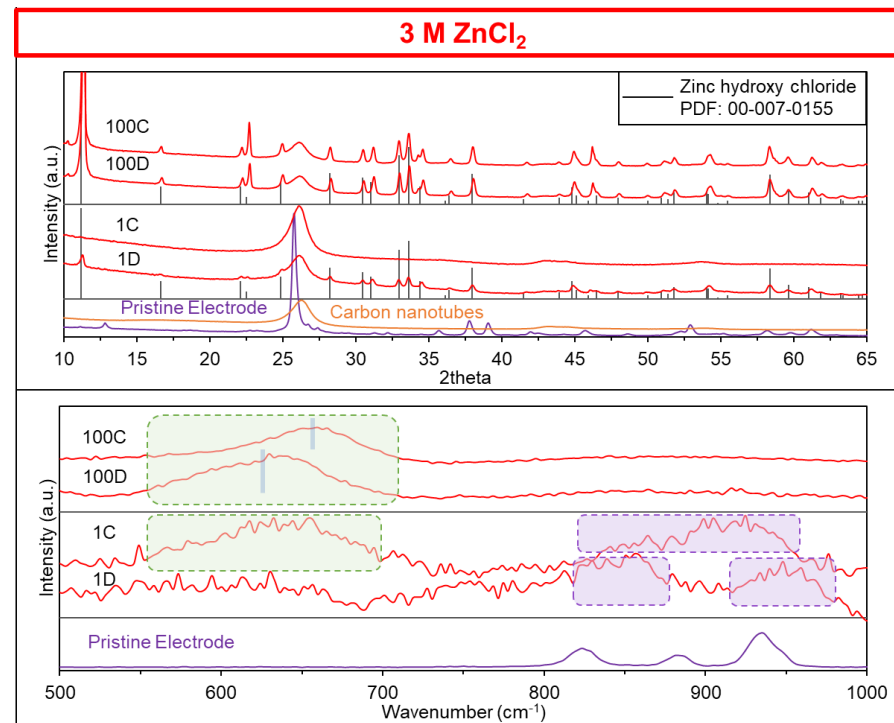
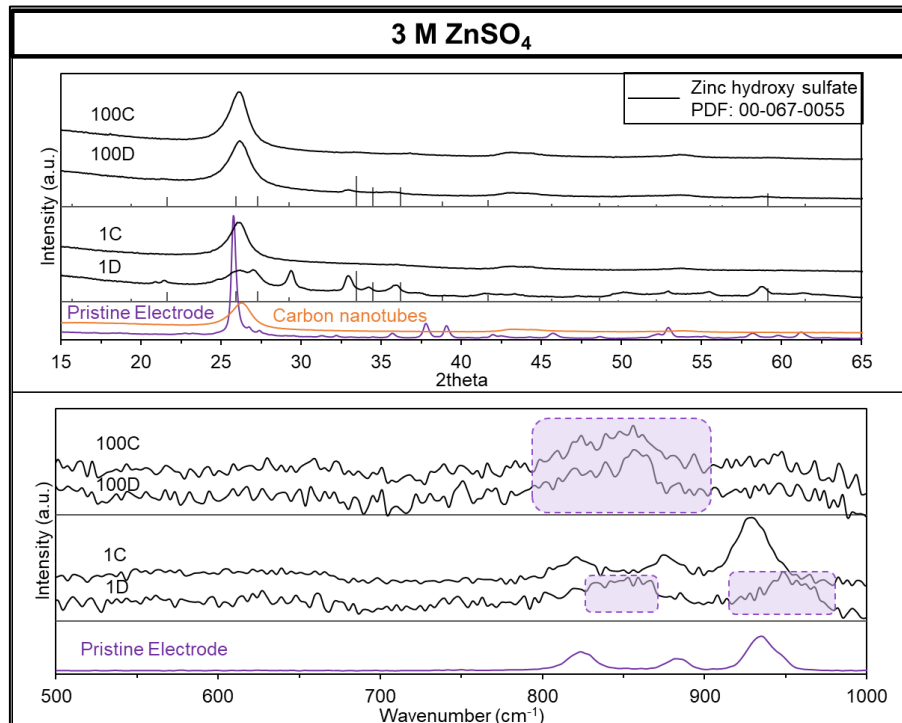
- Common strategy used to improve the cycling stability and capacity retention of manganese oxide cathodes in aqueous zinc anode batteries
- Similarly, with MnMoO_4 cathode, improved cycling stability and capacity retention was observed
- This is attributed to suppressed dissolution of the active material

Cycling at 100 and 500 mA/g and Voltage profiles

- Greater retention of both Mn and Mo 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 ZnSO₄ and ZnCl₂



X-ray Diffraction (XRD)

- Irreversible formation of zinc hydroxide by-products
 - Zn₄(SO₄)(OH)₆•3H₂O, zinc hydroxy sulfate (ZHS)
 - Zn₅(OH)₈Cl₂•H₂O, zinc hydroxy chloride (ZHC)
 - Commonly observed in other aqueous zinc systems with ZnSO₄ and ZnCl₂-based electrolytes

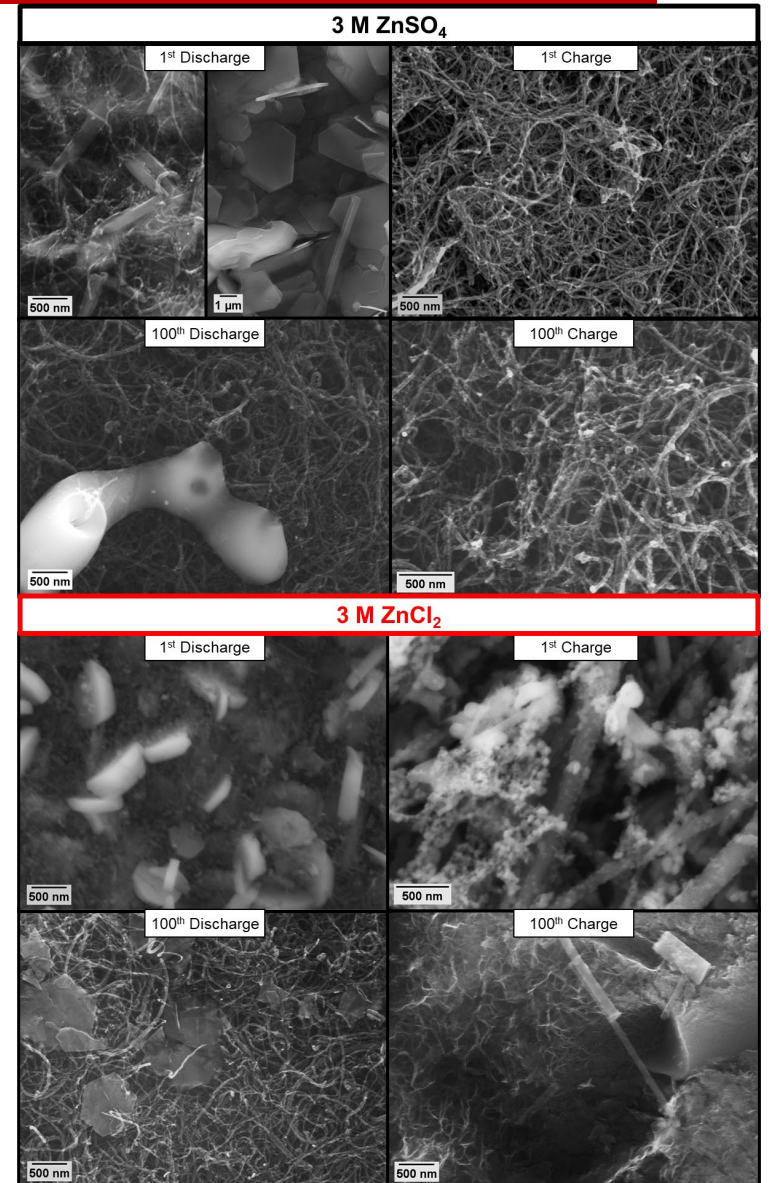
Raman Spectroscopy

- Retention of Mo-O signal in 3 M ZnSO₄
- Retention of Mn-O signals in 3 M ZnCl₂

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

Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)

- Initial porous nanorods dispersed in MWCNT matrix
- First discharge
 - Zn, O, Mo, S/Cl present
 - No Mn present (Mn dissolution in electrolyte)
- First charge
 - Zn, O, Mo, S/Cl, Mn present
 - Mn Deposition on MWCNT matrix
- 100th discharge
 - Zn, O, Mo, S/Cl present
 - No Mn present (Mn dissolution in electrolyte)
 - No longer has the dispersed solids observed in the first discharge
- 100th charge
 - Zn, O, Mo, S/Cl, Mn present (Less Mn in 3 M ZnSO_4 , Less Mo in 3 M ZnCl_2)
 - Deposition on MWCNT matrix, less
- Irreversible formation of zinc hydroxide by-products



Electron microscopy from Center for Functional Nanomaterials,
Brookhaven National Lab

Summary Zn/MnMoO₄ Aqueous Battery

Dual Redox Centers

- Mn^{2.5+}/Mn²⁺
- Mo⁶⁺/Mo⁴⁺

Anion-dependent reactions

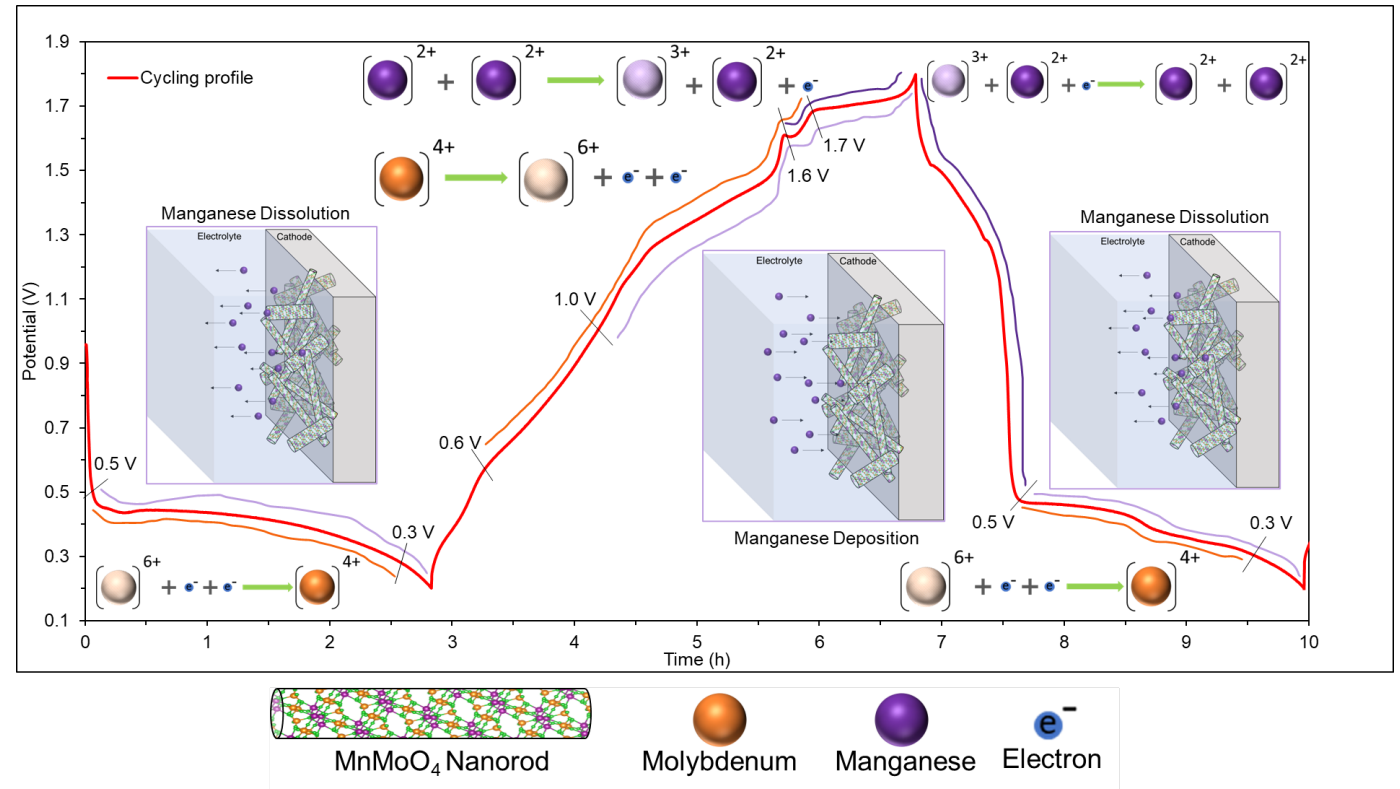
- SO₄²⁻ : greater retention of *Mo* redox
- Cl⁻ : greater retention of *Mn* redox
- Electrolyte anion and dissolved active material interactions
 - Stronger interactions between Mn²⁺ (aq) and SO₄²⁻ (aq) in the electrolyte compared to Cl⁻ (aq).
 - Hard-Soft Acid-Base theory
 - Solubility of the salts

Rate dependance

- Higher current: higher capacity in 3 M ZnSO₄
 - decreased dissolution of the MnMoO₄
 - retained the molybdenum redox which is dependent on solid material
- Lower current: higher capacity in 3 M ZnCl₂
 - 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



Acknowledgements



Dr. Imre Gyuk
Energy Storage Program Manager
Office of Electricity Delivery and Energy Reliability
U.S. Department of Energy



Dr. Babu Chalamala
Manager, Energy Storage Technology
and Systems Department
Sandia National Laboratories

Dr. Eric Spoerke
Energy Storage Materials Thrust Lead



The extended cycling experiments were supported by the U.S. Department of Energy, Office of Electricity, administered through Sandia National Laboratories, Purchase Order #1955692.

The materials synthesis and characterization were funded as part of the Center for Mesoscale Transport Properties, an Energy Frontier Research Center supported by the U.S. Department of Energy, Office of Science, under award #DE-SC0012673.

The electrolyte development and cell construction efforts were supported by Brookhaven National Laboratory.

Beamline 7-BM, quick x-ray absorption and scattering (QAS) of the National Synchrotron Light Source II, and.

Backup slides

Acetate Anion - Electrochemical Characterization: Rate capability and Cycling at 100 and 500 mA/g

- Zinc acetate is another commonly used electrolyte
- Limited by the solubility of the salt ($\sim 2\text{ M}$ @ 25°C)
- Rate capability displayed much lower capacities at higher current densities
- Fast fading at 100 mA/g
- Mn redox dominate
- Gradual increase at 500 mA/g

