Cycling and Failure Mechanisms of Rechargeable Alkaline Calcium Zincate ($CaZn_2(OH)_6 \cdot 2H_2O$) Anodes for Grid Storage Applications

Patrick K. Yang*[1,2,3], Damon E. Turney[3], Calvin D. Quilty[5], Timothy N. Lambert[5,6], Stephen O'Brien[1,2,3], Sanjoy Banerjee[3,4]

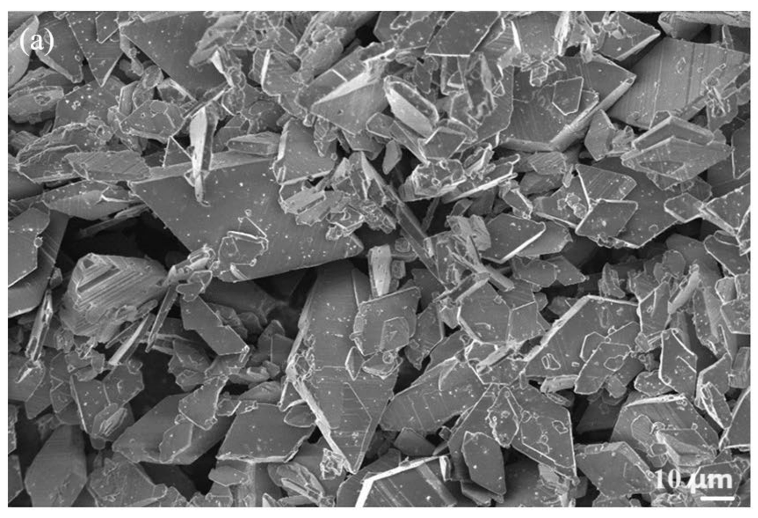
*pyang@gradcenter.cuny.edu

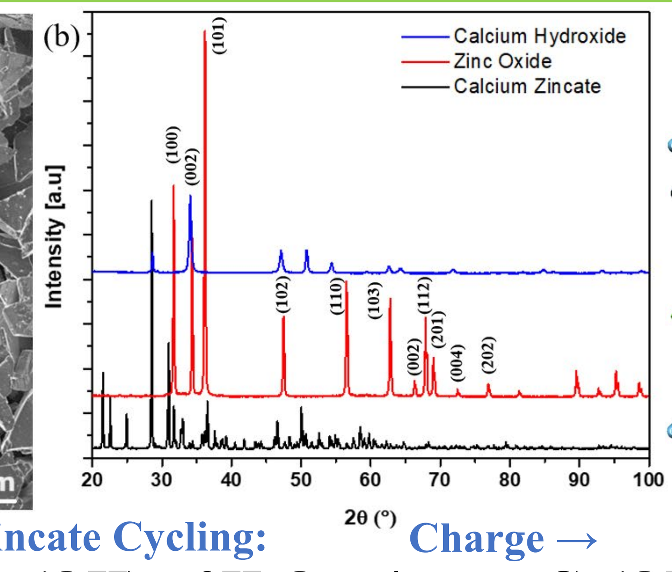
1. Ph.D. Program in Chemistry, The Graduate Center of the City University of New York
2. Department of Chemistry and Biochemistry, The City College of New York
3. The CUNY Energy Institute, The City College of New York
4. Department of Chemical Engineering, The City College of New York
5. Department of Photovoltaics and Materials Technology, Sandia National Laboratories
6. Center for Integrated Nanotechnologies, Sandia National Laboratories

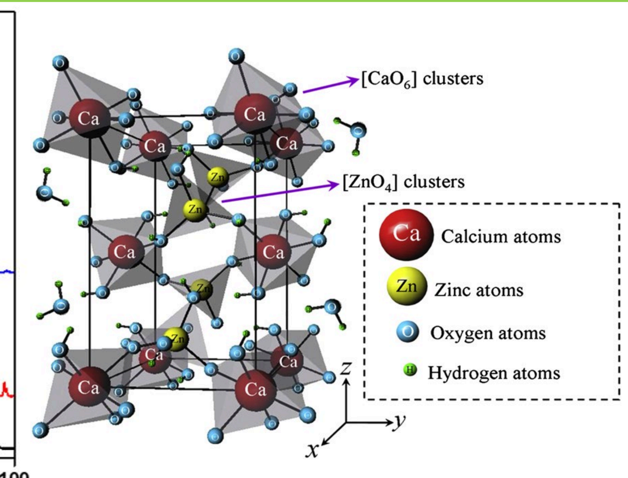
Background:

- Metallic zinc (Zn) is used industrially for primary and rechargeable Zn batteries such as Zn/Ni, Zn/Air, Ag/Zn, and Zn/MnO_2
- Zinc chemistry provides a high theoretical capacity, relative abundance, non-toxic, and non-flammable nature which make zinc batteries inherently safer for energy storage
- Failure mechanisms of zinc batteries include passivation, shape change/redistribution, dendrite formation, hydrogen evolution, and the crossover of zincate ($Zn(OH)_4^{2-}$) into the cathode
- Preliminary results indicate that anodes containing calcium zincate may mitigate some of these problems due to its low solubility in KOH electrolyte
- On charge the reaction product $Ca(OH)_2$ readily compounds with zincate ions to keep zincate concentrations low in the porous electrode material.

Calcium Zincate Synthesis Formation Reaction: $2\ Zn(OH)_4^{2-} + Ca(OH)_2 + 2H_2O \rightleftharpoons CaZn_2(OH)_6 \cdot 2H_2O + 4OH^-$







Calcium Zincate Cycling: Charge → / ← Discharge

$$CaZn_2(OH)_6 \cdot 2H_2O + 4e^- \rightleftharpoons Ca(OH)_2 + 2Zn + 4OH^- + 2H_2O$$

Project Goals – This research aims to understand the cycling and failure mechanisms of calcium zincate (CaZn) anodes, with the ultimate goal of developing methods to extend its cycle life.

Current Practice – There is limited research focused on cycling mechanism of CaZn anodes, with majority of efforts focused on improving electrical conductivity through additives or expensive current collector designs which add to manufacturing costs to improve CaZn cycle life.

Why The CUNY Energy Institute – CUNY Energy Institute has 15+ years of R&D expertise in rechargeable Zn battery systems and is at the forefront of Zn-MnO_2 batteries. Work done here resulted in a spinoff company, Urban Electric Power which has licensed the patented technology for commercialization and deployment into battery systems. This partnership provides a direct pathway to get our research findings to the market, accelerating the real-world adoption and impact.

Innovation – This work lays the groundwork to develop innovative methods for controlling the degradation mechanisms of CaZn anodes accomplished by postmortem analysis of CaZn anodes at different stages of cycling. A key finding is that during cycling, Zn migrates towards the center of the electrode surface. This segregation from calcium reduces the reversibility of CaZn formation, leading to performance degradation.

Impact – Discovering ways to extend cycle life of CaZn at high Zn utilization makes it an attractive replacement of Zn by driving cost down per cycle. The target cost of Zn-MnO_2 systems is \$50/kWh.

Alignment - Driving down the cost of Zn-MnO_2 batteries ensures reliable, affordable, and safe energy storage for American homes and businesses while improving grid resilience and transforming infrastructure without substantial new investment.

Rough Estimate on Raw Materials Cost at Scale*

Rough Bill of Materials (BOM) Cost at Scale - Estimated from Publicly Available info on Alibaba.com

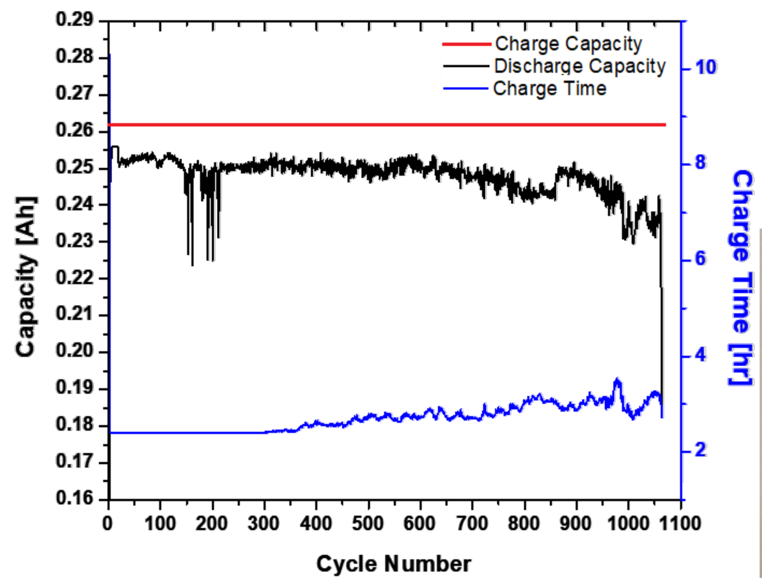
Zn (\$/kg)	ZnO (\$/kg)	Rough Estimate of Calcium Zincate based on starting materials (\$/kg)	Bi_2O_3 (\$/kg)	$Ca(OH)_2$ (\$/kg)	PTFE Dispersion 60 wt.% Solids in water (\$/kg)	25 wt.% KOH (\$/kg)
4.06	1	1.71	8	0.3	9.43	0.95

Rough Cost to Manufacture Tetragonal Calcium Zincate Based on Sharma Recipe

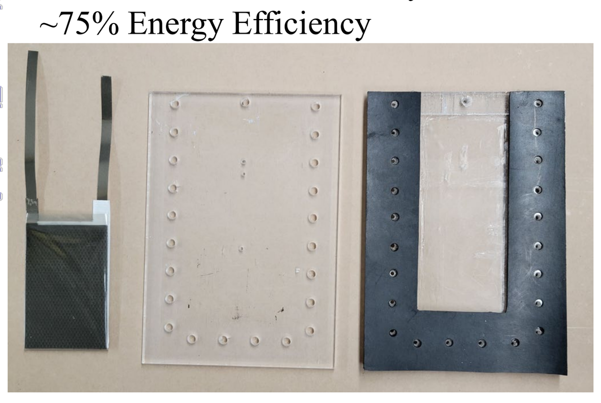
	Zinc Oxide (ZnO)	Calcium Hydroxide ($Ca(OH)_2$)	Potassium Hydroxide (KOH)	Deionized Water	Calcium Zincate (CaZn)
kg	23	10	100	14.6	35
\$	23	3	11.23	14.6	51.83

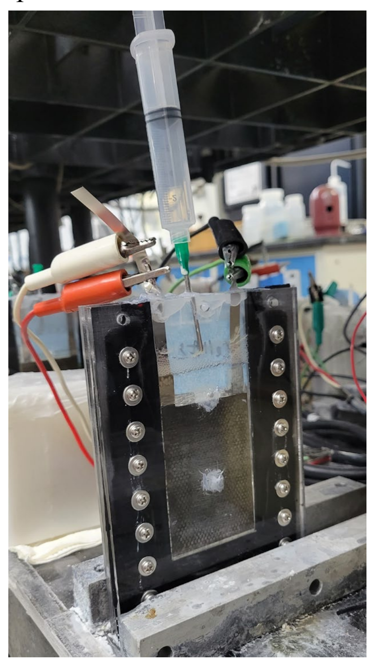
* Raw material cost information was all obtained publicly from multiple vendors on www.Alibaba.com. Calcium zincate price estimated assuming 20% KOH can be recycled at 90% of the fresh KOH cost, DI water treatment cost \$0.5/L, additional cost of factory labor, energy, and equipment is 15% on top of the total materials cost

Preliminary Experiments Cycling Results



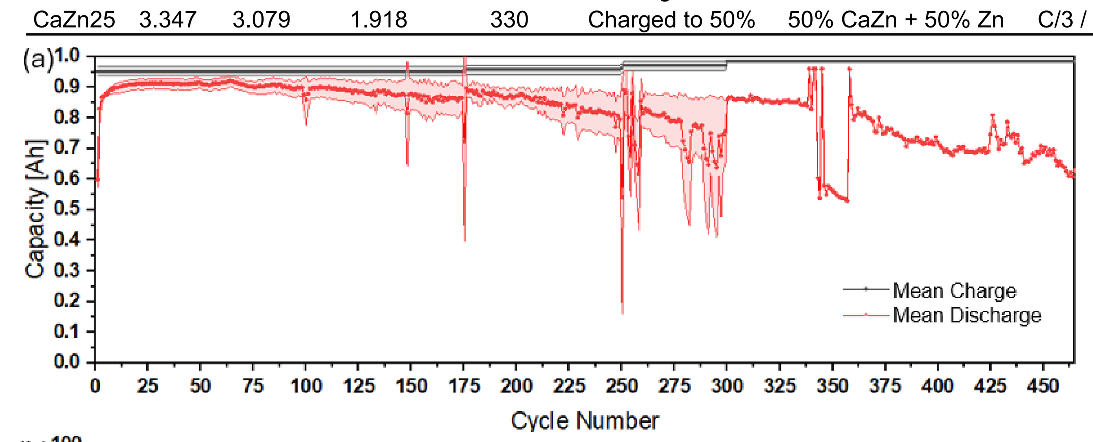
86 wt.% CaZn/10 wt.% Carbon/ 4 wt.% PTFE with 20% KOH ZnO Saturated
C/3 at 20% utilization of theoretical Zn
Achieved 1000+ cycles
~91% Coulombic Efficiency
~75% Energy Efficiency

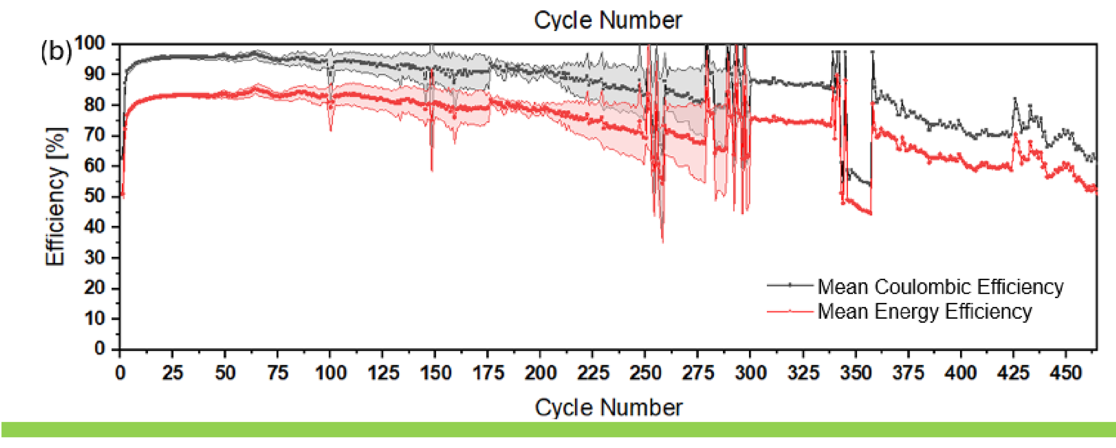




Replicate CaZn Cells: 50% Zinc Utilization Anode

Cell Name	Sheet 1 Mass (g)	Sheet 2 Mass (g)	Total Theoretical Capacity (Ah)	Stopped Cycle #	Stopped State of Charge and Theoretical % Zn Utilization	Theoretical Final Anode Composition	C-rate (charge/ discharge)
CaZn1	3.131	3.072	1.856	249	Discharged to 0%	100% CaZn	C/3 / C/3
CaZn2	3.146	3.140	1.881	175	Discharged to 0%	100% CaZn	C/3 / C/3
CaZn3	3.143	3.058	1.850	250	Charged to 50%	50% CaZn + 50% Zn	C/3 / C/3
CaZn4	3.170	3.100	1.870	175	Charged to 50%	50% CaZn + 50% Zn	C/3 / C/3
CaZn5	3.084	3.118	1.851	300	Discharged to 0%	100% CaZn	C/3 / C/3
CaZn16	3.115	3.084	1.850	175	Discharged to 0%	100% CaZn	C/3 / C/3
CaZn25	3.347	3.079	1.918	330	Charged to 50%	50% CaZn + 50% Zn	C/3 / C/3





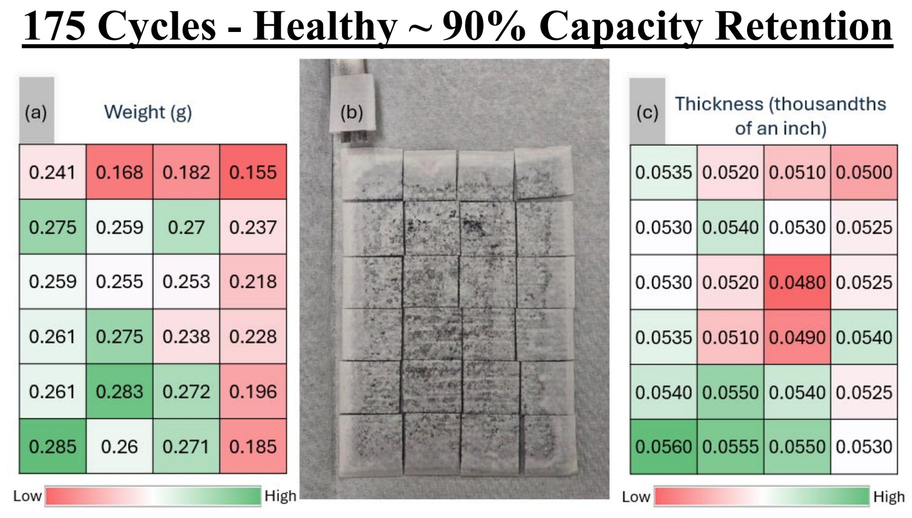
- Replicate CaZn Cells were cycled and stopped at different states of charge.

- The dark black and red lines show the average/ mean value of the cycled tests, and the shaded areas represent are one standard deviation away from the mean.

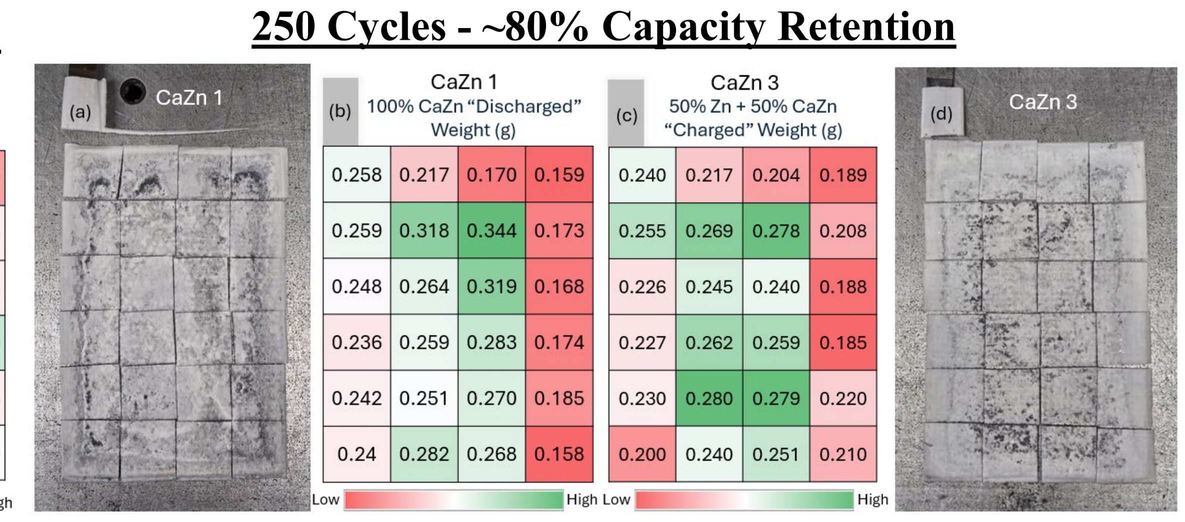
- Cells show good replicability for the first ~150 cycles but then the cycling deviation between cells increases

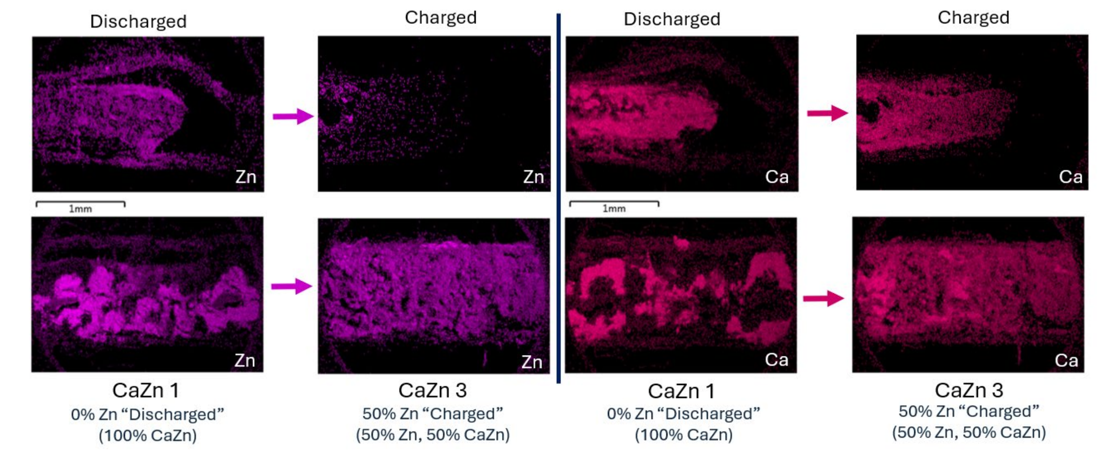
Cycling Analysis Results

175 Cycles - Healthy ~ 90% Capacity Retention



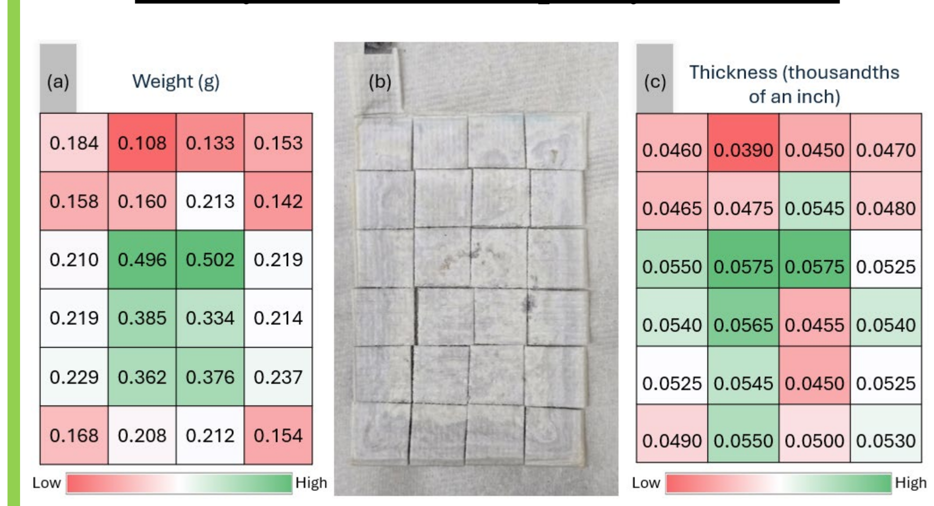
250 Cycles - ~80% Capacity Retention

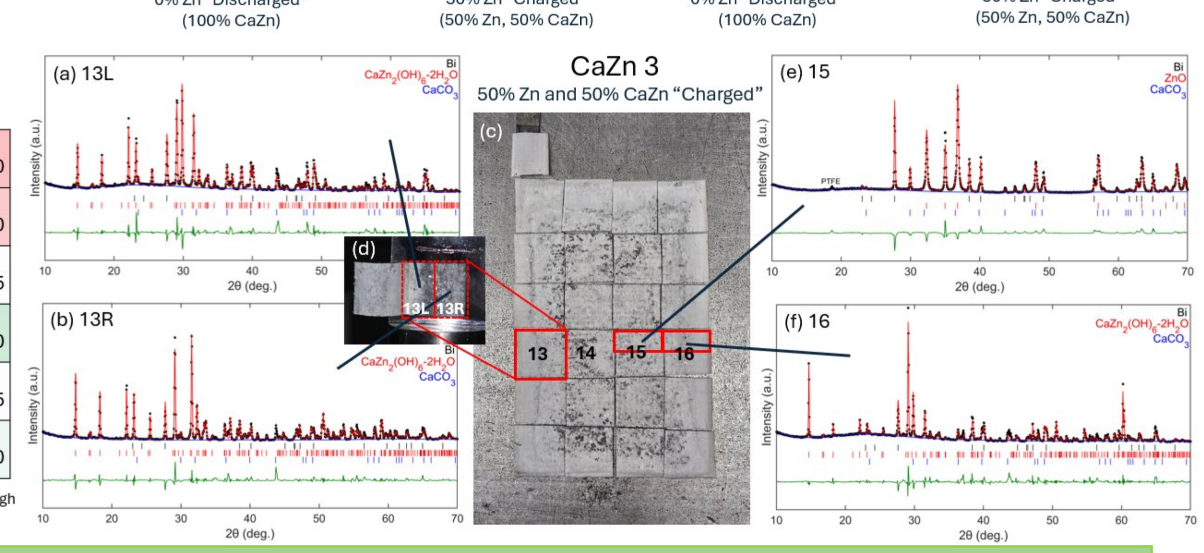


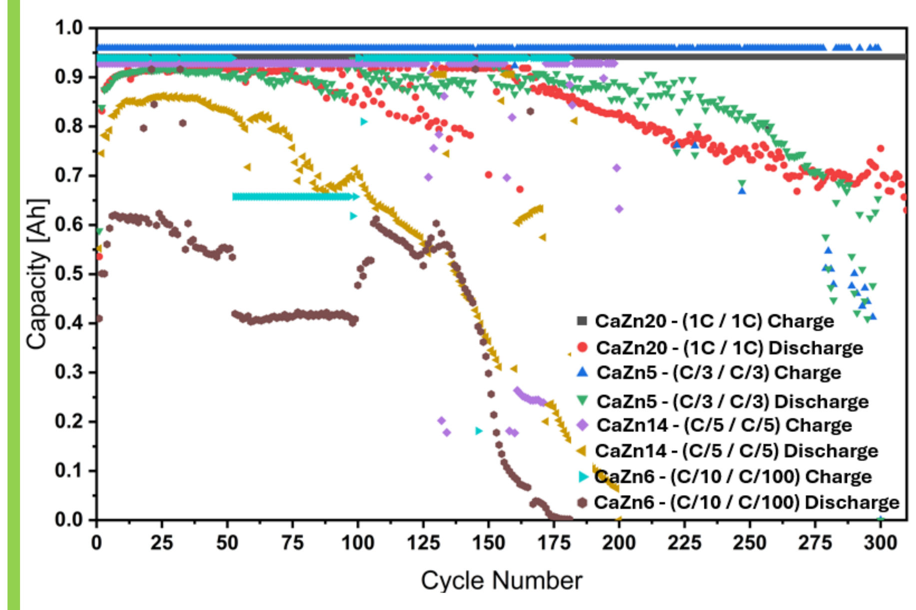


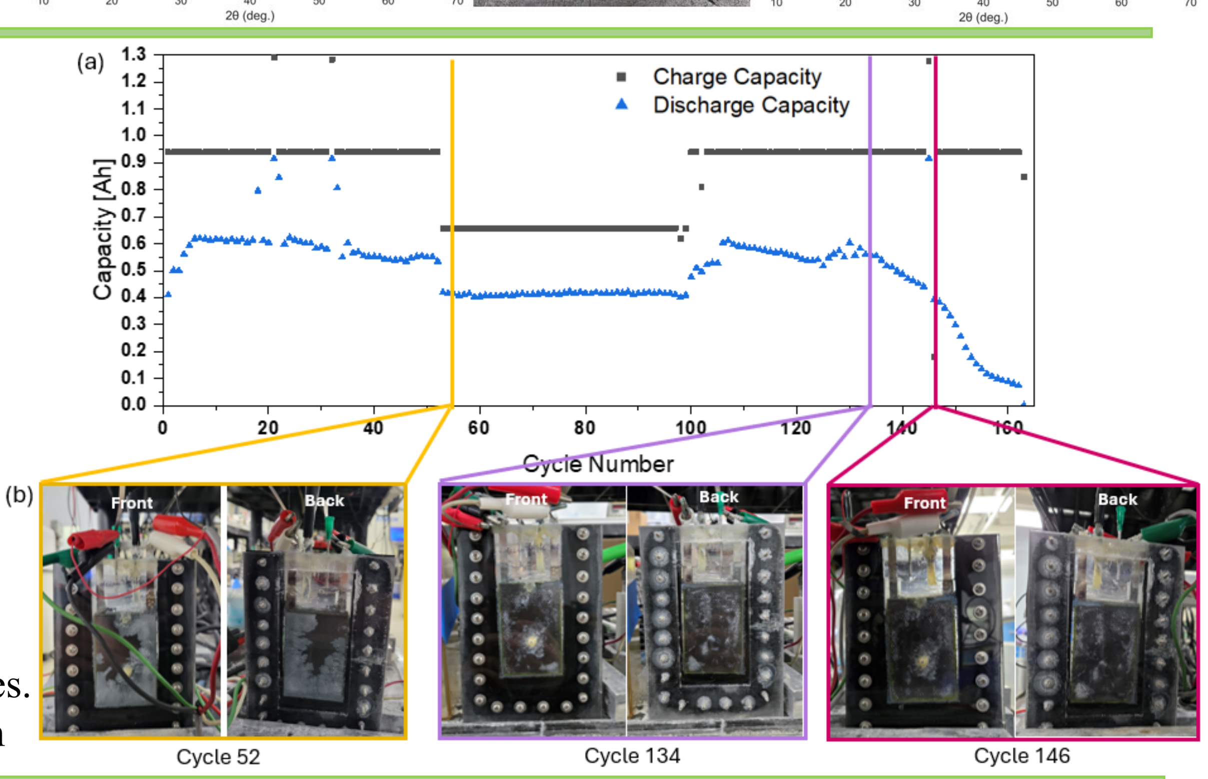
- As CaZn anodes cycle, the mass and thickness in the center of the electrode increases while the edges decrease.
- Looking at cross-sectional SEM-EDX, Zn is migrating to more conductive areas leading to segregation from Ca.
- The very edge of the anodes show a loss of Zn but well distributed internally during the "charged" state.

300 Cycles - ~70% Capacity Retention

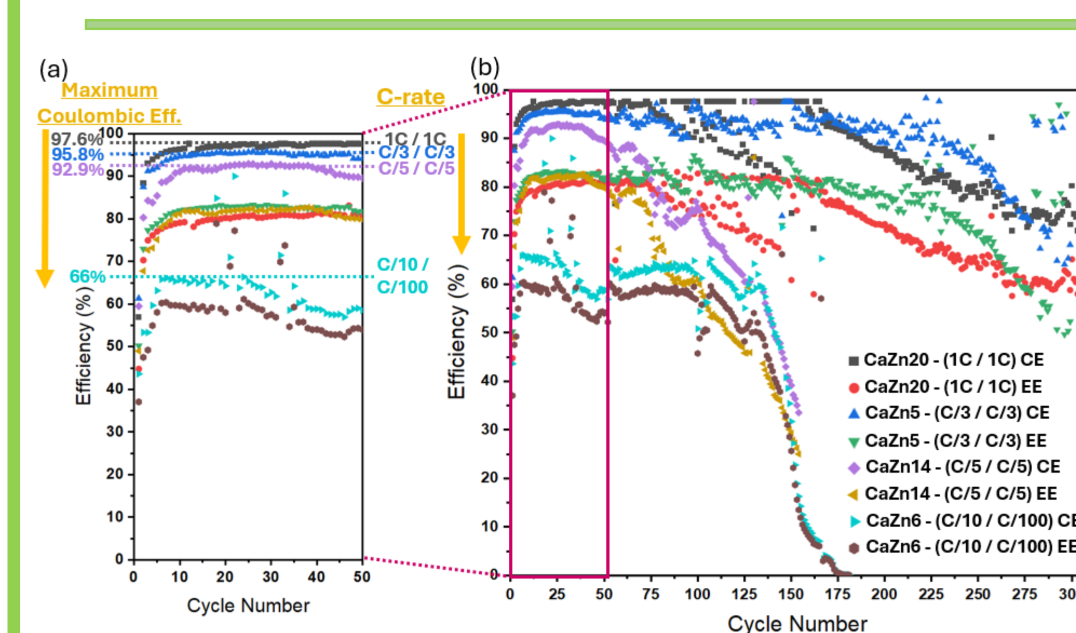


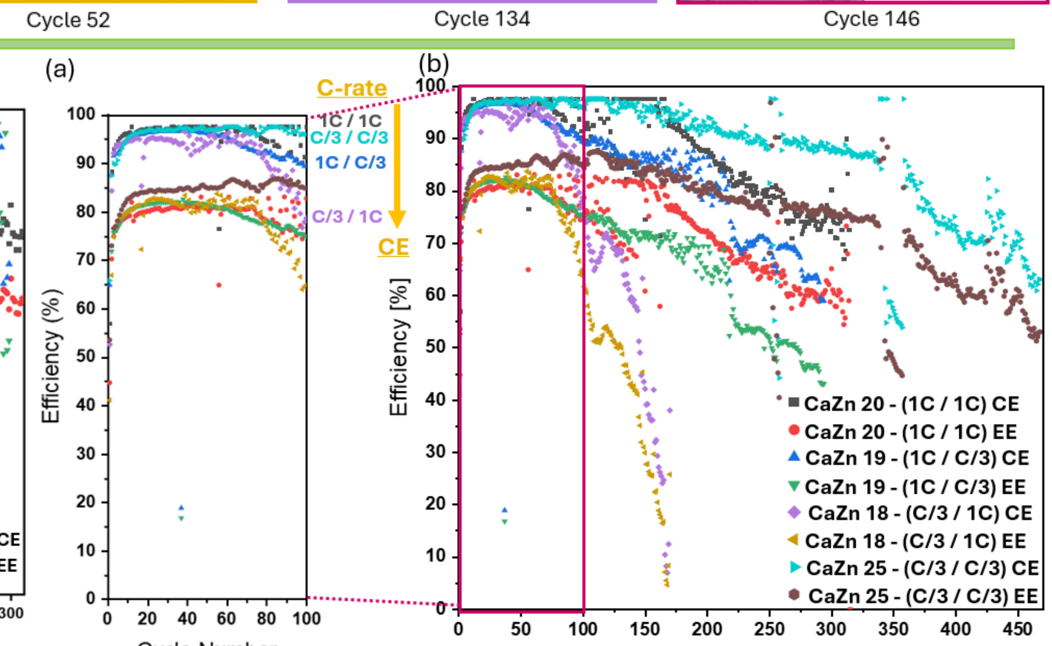






- As you decrease the c-rate, CaZn cycle life decreases.
- Slower CaZn cycling results in visible Zn migration





- The maximum achievable coulombic and energy efficiency decreases as you lower the c-rate.
- Slow c-rates show dramatic deterioration in cycling efficiency and performance

- For optimized CaZn cycling, it is important to have matching charge and discharge c-rates.
- Having a faster charge rate (1C) and slower discharge (C/3) is better than a slow charge (C/3) and fast discharge (1C).

Conclusions/ Future Directions

- The overall cycle life of CaZn anode is heavily dependent on the c-rate that it is cycled at.
- During cycling, Zinc migrates towards the surface middle of the electrode away from the Calcium which reduces the overall reversibility of CaZn reformation and leads to overall performance degradation.
- Consider additional additives and methods to improve cycling performance and extend cycle life of CaZn
- Investigating optimal conditions for full cell testing of CaZn vs MnO_2

References: **(1)** P.K. Yang et.al. Under Submission *EES Batteries* (2025) **(2)** P.K. Yang et.al. *Energy Advances* (2024) **(3)** R. A. Sharma *J. Electrochem. Soc.* 133 (**1986**) 2215 **(4)** J. Yu et. al. *J. Power Sources* 103 (**2001**) 93-97 **(5)** J. Hao et. al. *J. Electrochem Soc.* 161 (5) (**2014**) A704-A707 **(6)** E. Shangguan et. al. *J. Alloy Compd.* Vol 853 (5) (**2021**) 156965

Acknowledgements: This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. The views expressed in this article do not necessarily represent the views of the U.S. Department of Energy or the United States Government. This article has been authored by an employee of National Technology & Engineering Solutions of Sandia, LLC under Contract No. DE-NA0003525 with the U.S. Department of Energy (DOE). The National Technology & Engineering Solutions of Sandia, LLC employee owns all right, title and interest to their contribution to the article and is responsible for its contents. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this article or allow others to do so, for United States Government purposes. The DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan https://www.energy.gov/downloads/doe-public-access-plan."