Understanding the Role of Calcium Zincate ($Ca[Zn(OH)_3]_2 \cdot 2H_2O$) in Improving Cycle Life and Performance in Rechargeable Alkaline Zinc Batteries

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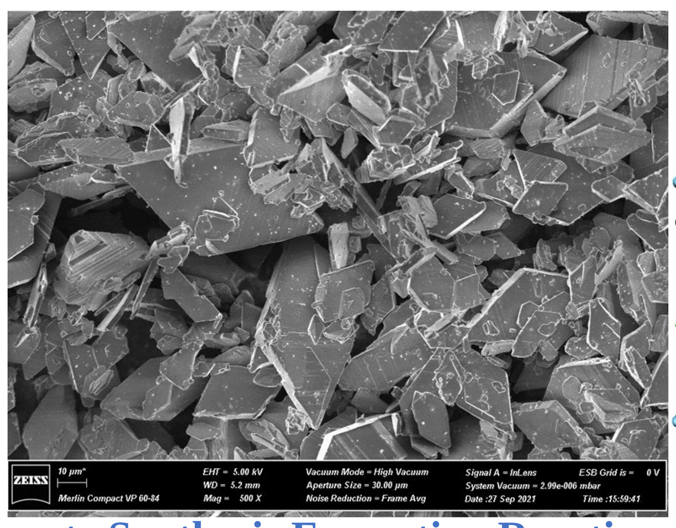
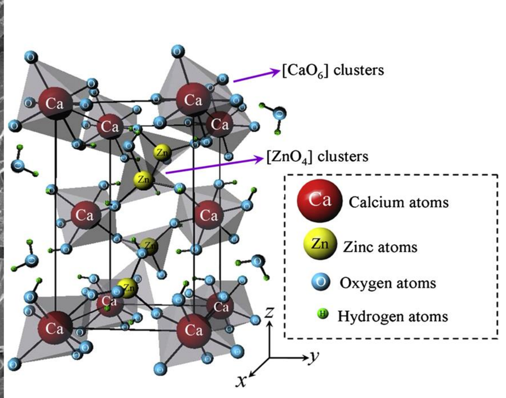
Objective: Understand the role of Calcium Zincate on the cycling performance of mixed anodes at high utilization of zinc.

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

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

Rough Estimate on Raw Materials Cost at Scale*

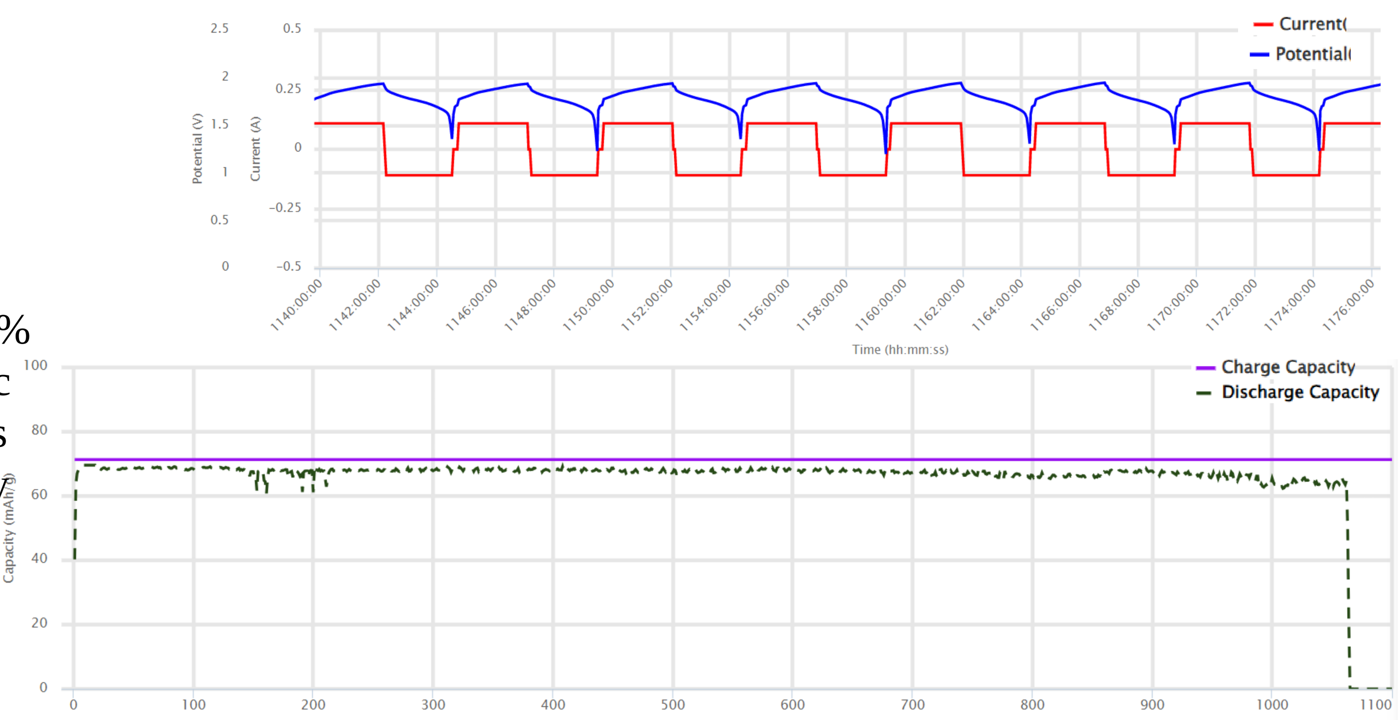
Metallic Zinc (Zn) ($/kg)	Zinc Oxide (ZnO) ($/kg)	Calcium Zincate Rough Estimate ($/kg)	Bismuth Oxide (Bi_2O_3) ($/kg)	Carbon ($/kg)	Calcium Hydroxide ($Ca(OH)_2$) ($/kg)	PTFE Dispersion Teflon ($/kg)	25% Potassium Hydroxide (KOH) ($/kg)
5	3	3.2	10	3	0.3	7	1.2

	Scaled Up Sharma Calcium Zincate Standard RT Recipe				
	ZnO (kg)	**Ca(OH)2** (kg)	**20% KOH** (kg)	**DI Water** (L)	**Calcium Zincate** (kg)
kg/L	23	10	100	14.6	35
$	69	3	11.35	14.6	3.2

***** 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.% Calcium Zincate/
10 wt.% Carbon Black/
4 wt.% PTFE
20% KOH ZnO Saturated
Anode cycled fast C/3 at 20% utilization of theoretical zinc
Achieved over 1000+ cycles
~91% Coulombic Efficiency
~75% Energy Efficiency

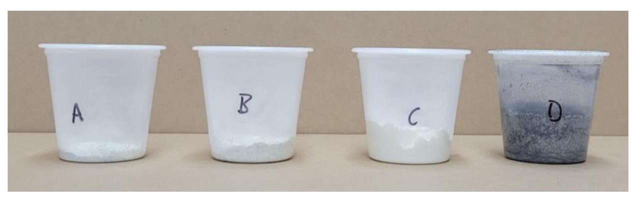


Design of Experiments: 50% Zinc Utilization Anode Compositions

Cell #	Anode Composition in wt.%	Metallic Zinc (g)	Calcium Zincate (g)	10 wt.% Bi_2O_3 (g)	4 wt.% PTFE (g)	moles of Zinc	Total mass (g)	Active material (g)	Rough Cost of Anode ($/kg)	# of Cycles to 70% Capacity	Specific Energy Density (Wh/kg)	$/kg/kWh/ #Cycles to 70% Capacity
0	Zinc Anode 96% Zn	9.03	0.00	0.00	0.36	0.14	9.5	9.03	47.65	—	—	—
0	Baseline 86% Zinc + 10% Bi_2O_3	9.03	0.00	1.05	0.42	0.14	10.5	9.03	58.59	—	—	—
1	60% Zn + 26% Cal Zinc + 10% Bi_2O_3	7.62	3.30	1.21	0.48	0.14	12.7	10.92	64.98 (1.1 x Baseline)	66	56.9	18.53
2	26% Zn + 60% Cal Zinc + 10% Bi_2O_3	4.58	10.56	1.67	0.67	0.14	17.6	15.14	79.39 (1.4 x Baseline)	137	41.0	7.08
3	86% Cal Zinc + 10% Bi_2O_3	0.00	21.33	2.36	0.94	0.14	24.8	21.33	100.38 (1.7 x Baseline)	282	29.0	2.65
4	86% Cal Zinc + 10% Carbon	0.00	21.33	2.36	0.94	0.14	24.8	21.33	83.02 (1.4 x Baseline)	215	28.7	2.91

Electrode Mixture Composition and Properties

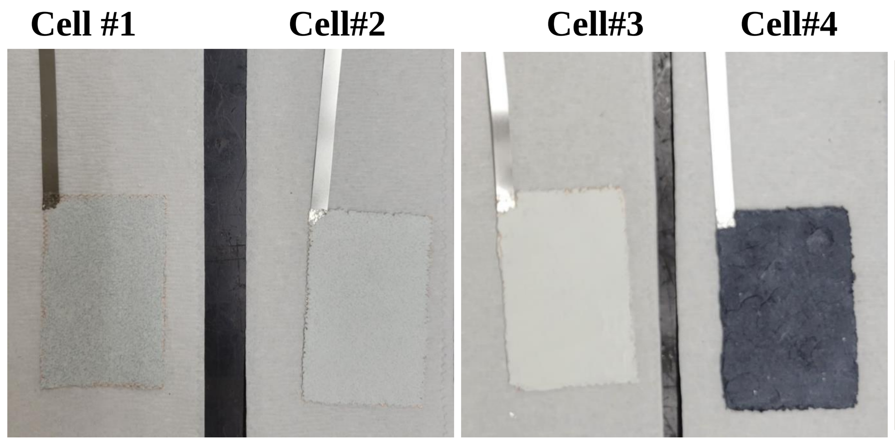
Material	Density (g/cm^3)	Volume Expansion vs. pure Zn
Metallic Zinc	7.133	1
Zinc Oxide	5.61	1.27
Calcium Zincate	2.59	2.75

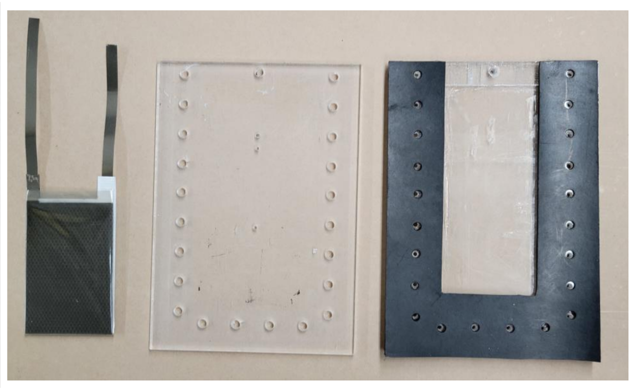


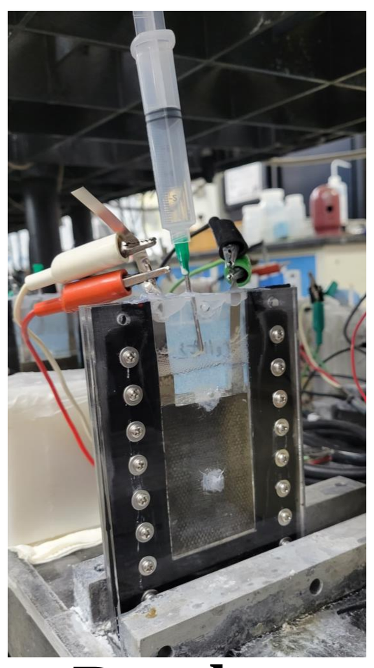
Cell #1 Cell#2 Cell#3 Cell#4

2 x 3 in Anode vs SiNi Fabrication

Cell #1 Cell#2 Cell#3 Cell#4



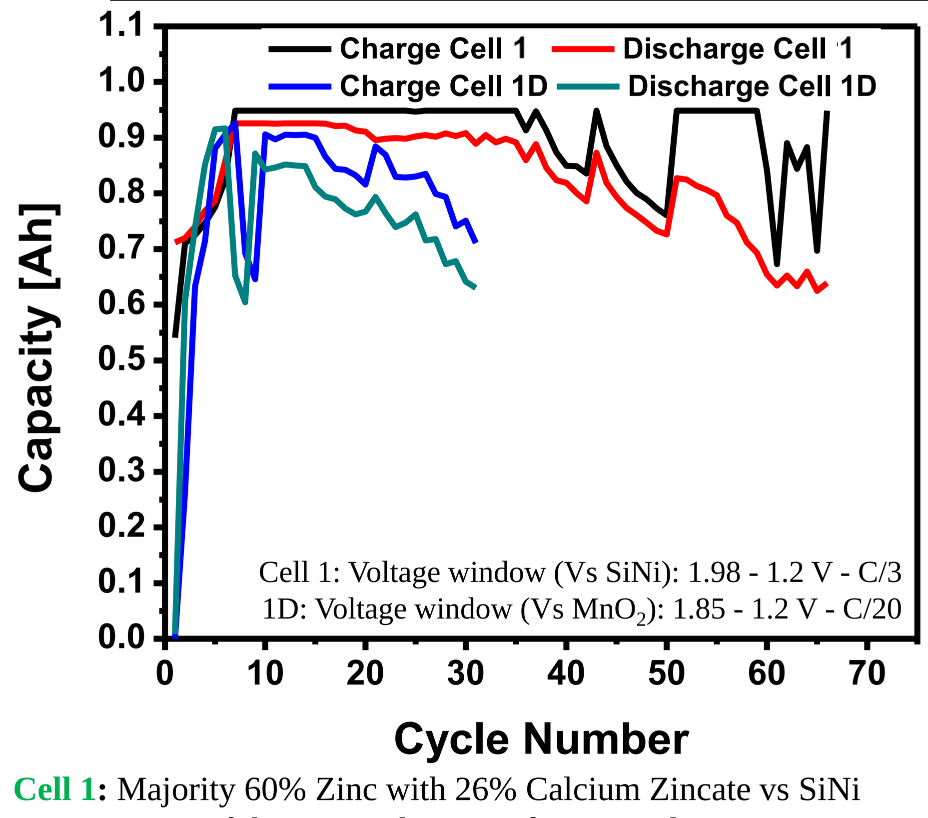


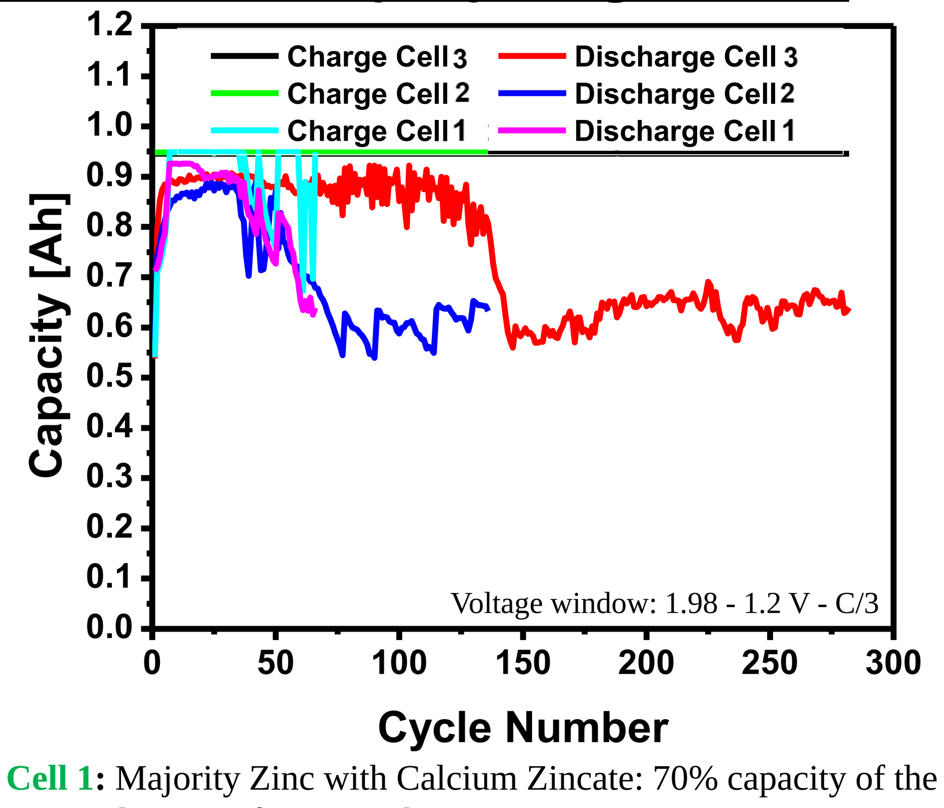


Anode Thickness (thousandths of an inch)

Cell #1: 0.0155 - 0.0170 thou **Cell #2:** 0.0240 - 0.0275 thou
Cell #3: 0.0390 - 0.0425 thou **Cell #4** 0.0400 - 0.0520 thou

50% Zinc Utilization in 20% KOH - Battery Cycling Results

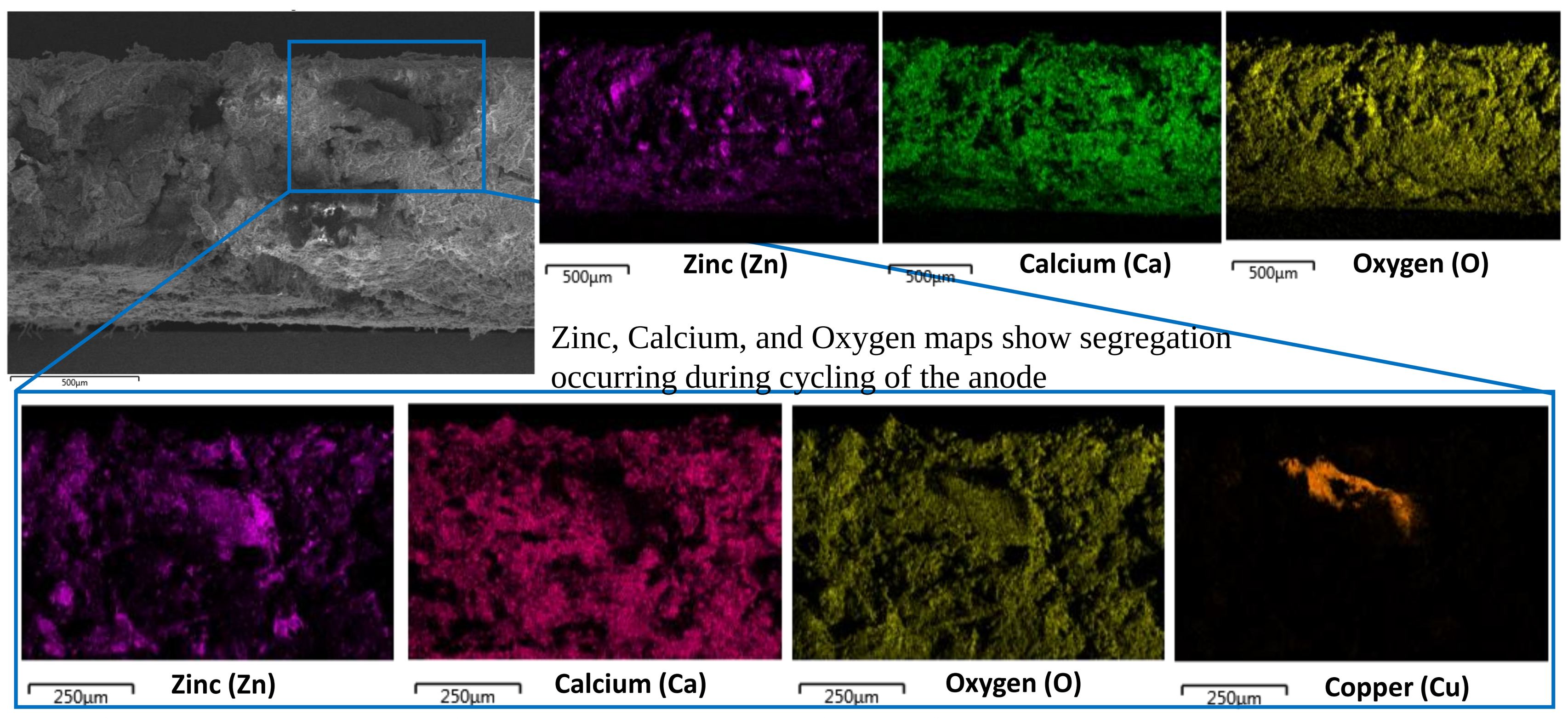




Cell 1: Majority 60% Zinc with 26% Calcium Zincate vs SiNi 70% capacity of the 50% utilization after 66 cycles Average CE: 93%, EE: 81%
Cell 1D: Majority 60% Zinc with 26% Calcium Zincate vs MnO_2 70% capacity of the 50% utilization after 31 cycles Average CE: 94%, EE: 82%

Cell 1: Majority Zinc with Calcium Zincate: 70% capacity of the 50% utilization after 66 cycles -Average CE: 93%, EE: 81%
Cell 2: Majority Calcium Zincate with Zinc: 70% capacity of the 50% after 137 cycles -Average CE: 74%, EE: 59%
Cell 3: Pure 86% Calcium Zincate: 70% capacity of the 50% utilization after 282 cycles -Average CE: 79%, EE: 65%

SEM-EDX Mapping of Failed Pure Calcium Zincate Anode (Charged State)



Zinc, Calcium, and Oxygen maps show segregation occurring during cycling of the anode

Preliminary Conclusions/ Future Directions

- Various formulations of metallic Zinc and Calcium Zincate were cycled at high 50% utilization of the total zinc to understand the role that Calcium Zincate plays in improving battery performance
- Zinc anode cycling performance increases when adding Calcium Zincate which mitigates shape change
- Will investigate the reaction pathways of Calcium Zincate during cycling at the nanoscale that led to the improved material utilization at high cycle life compared to metallic zinc
- Will investigate hydrogen evolution reaction (HER) and possible additives to reduce zinc anode gassing

References: (1) R. A. Sharma *J. Electrochem. Soc.* 133 (**1986**) 2215 **(2)** J. Yu et. al. *J. Power Sources* 103 (**2001**) 93-97 **(3)** J. Hao et. al. *J. Electrochem Soc.* 161 (5) (**2014**) A704-A707 **(4)** E. Shangguan et. al. *J. Alloy Compd.* Vol 853 (5) (**2021**) 156965

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