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Studying the Addition of Metallic Zinc (Zn) to Rechargeable Alkaline Calcium Zincate ($Ca[Zn(OH)_3]_2 \cdot 2H_2O$) Anodes

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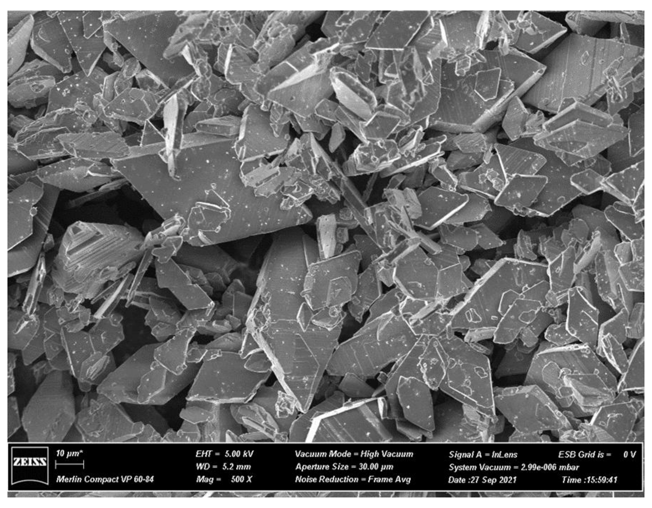
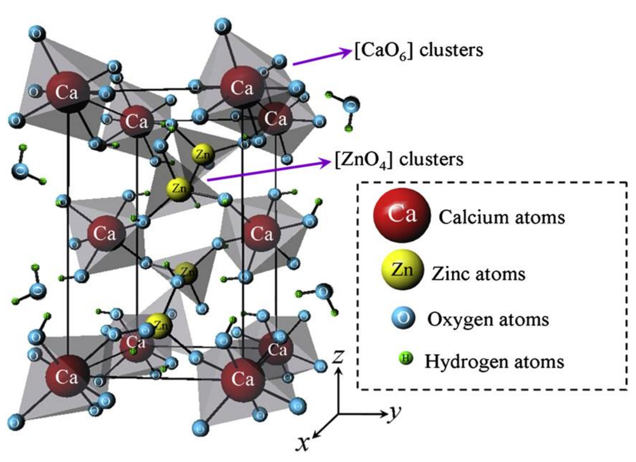
Objective: Understand the role of various additives on the cycling performance of calcium zincate anodes at high utilization of the zinc.

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 them 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.





$$2\,Zn(OH)_4^{2-} + Ca(OH)_2 + 2H_2O \rightleftharpoons CaZn_2(OH)_6 \cdot 2H_2O + 4OH^-$$

$$CaZn_2(OH)_6 \cdot 2H_2O + 4e^- \underset{\leftarrow \text{ Discharge}}{\overset{\text{Charge} \rightarrow}{\rightleftharpoons}} Ca(OH)_2 + 2Zn + 4OH^- + 2H_2O$$

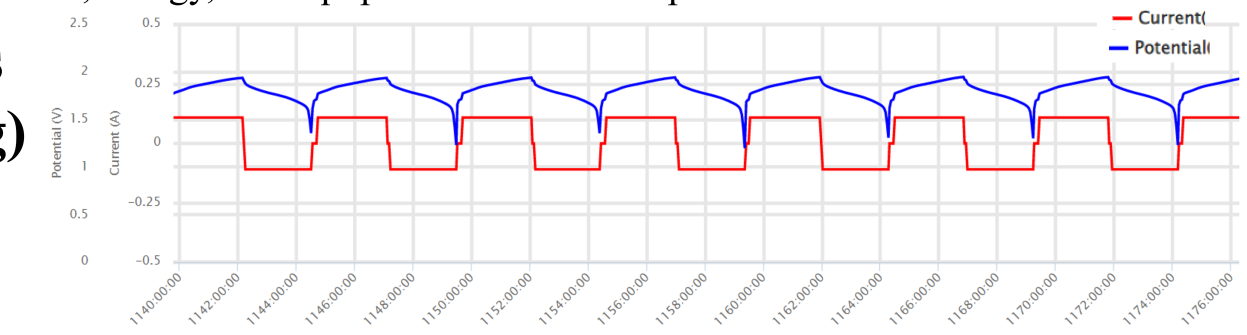
Rough Estimate on Raw Materials Cost at Scale*

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

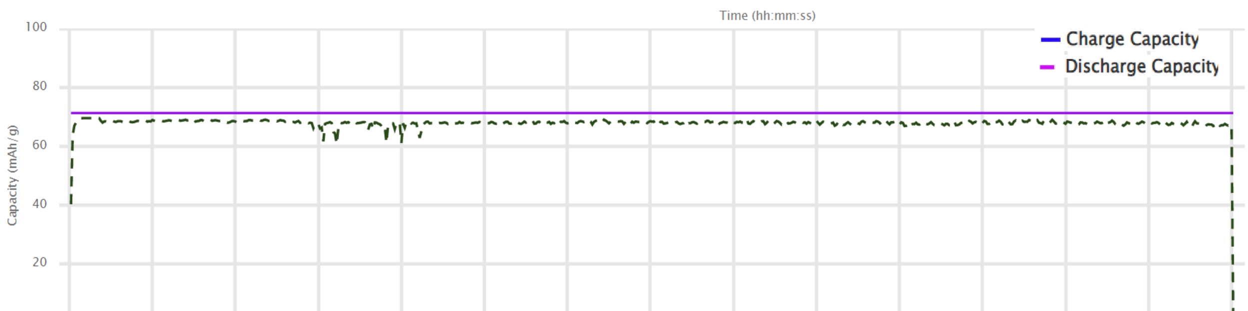
	Scaled Up Sharma Calcium Zincate Standard RT Recipe				
	ZnO (kg)	**Ca(OH)2** (kg)	**20% KOH** (kg)	**DI Water** (L)	**Calcium Zincate** (kg)
kg/L	23	10	100	14.6	35
$	69	3	11.35	14.6	3.2

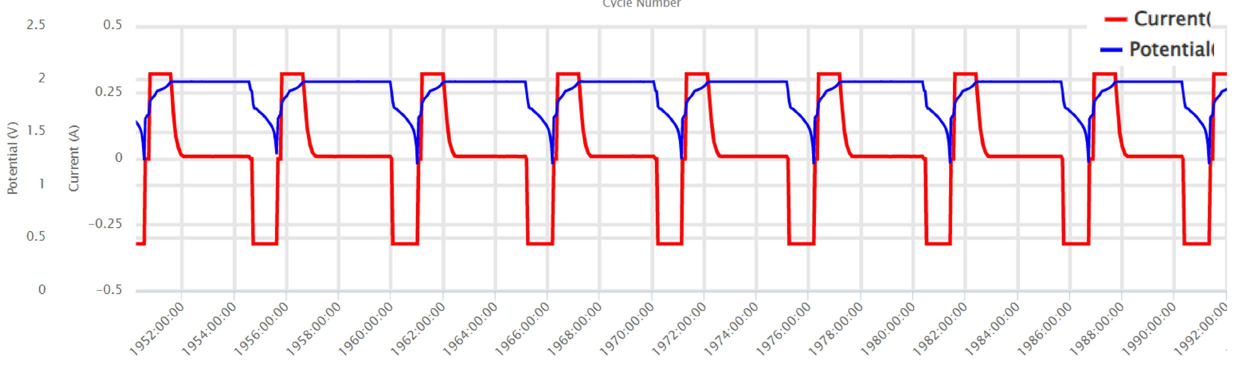
* Raw material cost information was all obtained publicly from multiple vendors on www.Alibaba.com. Calcium zincate price estimated assuming 20% KOH can be recycled at 90% of the fresh KOH cost, DI water treatment cost $0.5/L, additional cost of factory labor, energy, and equipment is 15% on top of the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

Preliminary Experiments Cycling Results (Ongoing)

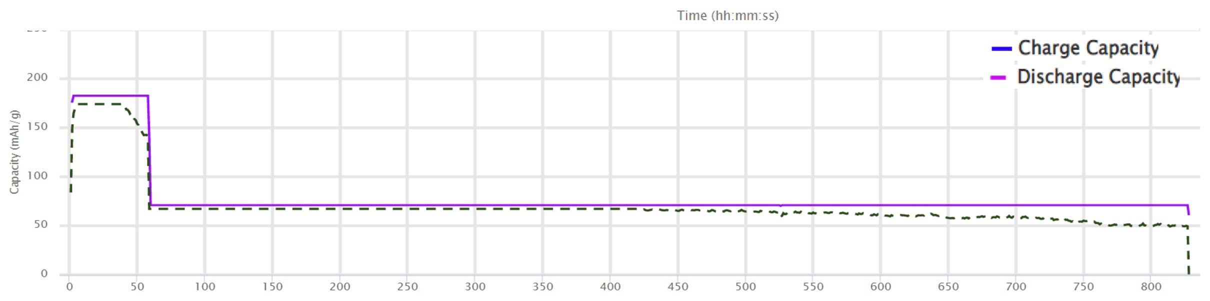


86 wt.% Calcium Zincate/ 10 wt.% Carbon Black/ 4 wt.% PTFE Anode currently cycling fast at 20% utilization of zinc





86 wt.% Calcium zincate/ 10 wt.% Bi_2O_3 / 4 wt.% PTFE Anode currently cycling fast at 50% utilization of zinc for around 50 cycles before being reduced to 25% utilization of zinc

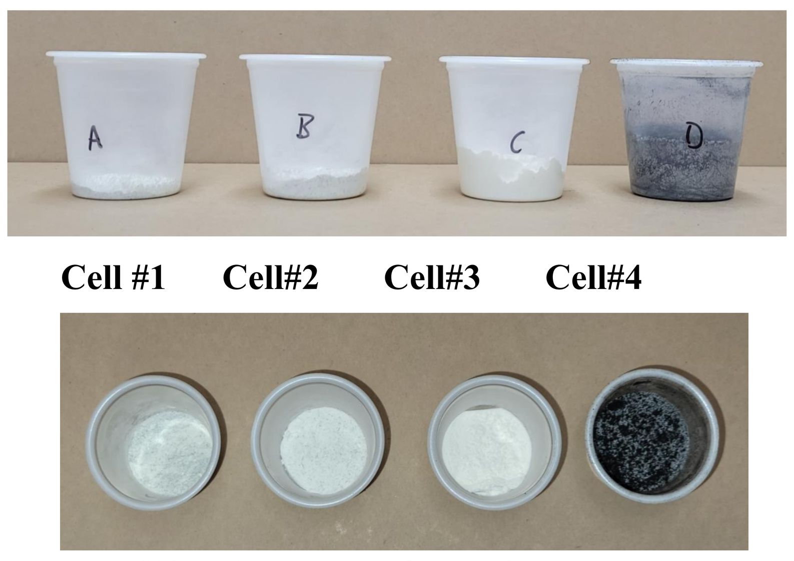


Design of Experiments: Anode Compositions

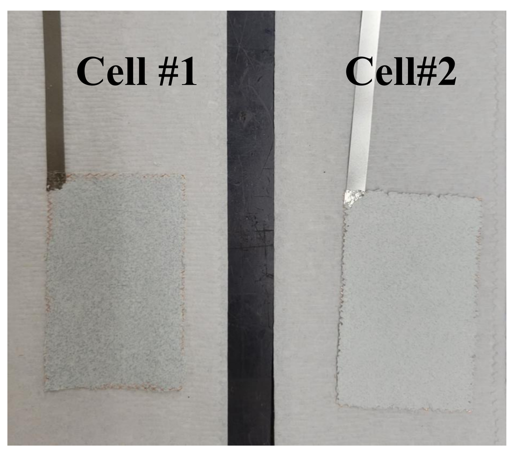
Total mass (g)	Active material (g)	Anode Composition in wt.%	Cell #	Metallic Zinc (g)	Calcium Zincate (g)	10 wt.% Bi_2O_3 (g)	4 wt.% PTFE (g)	moles of Zinc	g of zinc total	% of Zinc Utilization	Rough Cost of Anode ($/kg)
9.5	9.03	Zinc Anode 96% Zn	0	9.03	0.00	0.00	0.36	0.14	9.03	50.0%	47.65
10.5	9.03	Baseline 86% Zinc + 10% Bi_2O_3	0	9.03	0.00	1.05	0.42	0.14	9.03	50.0%	58.59
12.7	10.92	60% Zn + 26% Cal Zinc + 10% Bi_2O_3	1	7.62	3.30	1.21	0.48	0.14	9.02	50.0%	64.98 (1.1 x Baseline)
17.6	15.14	26% Zn + 60% Cal Zinc + 10% Bi_2O_3	2	4.58	10.56	1.67	0.67	0.14	9.05	50.0%	79.39 (1.4 x Baseline)
24.8	21.33	86% Cal Zinc + 10% Bi_2O_3	3	0.00	21.33	2.36	0.94	0.14	9.03	50.0%	100.38 (1.7 x Baseline)
24.8	21.33	86% Cal Zinc + 10% Carbon	4	0.00	21.33	2.36	0.94	0.14	9.03	50.0%	83.02 (1.4 x Baseline)

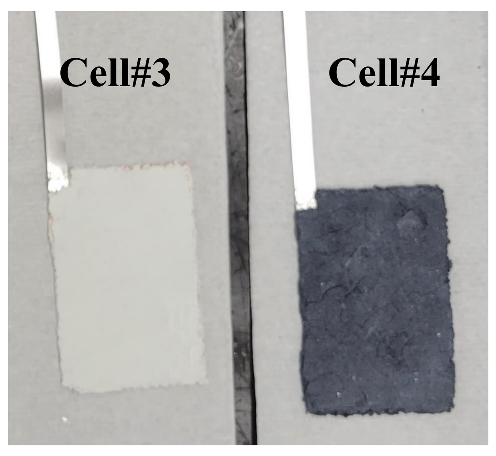
Electrode Mixture Composition and Properties

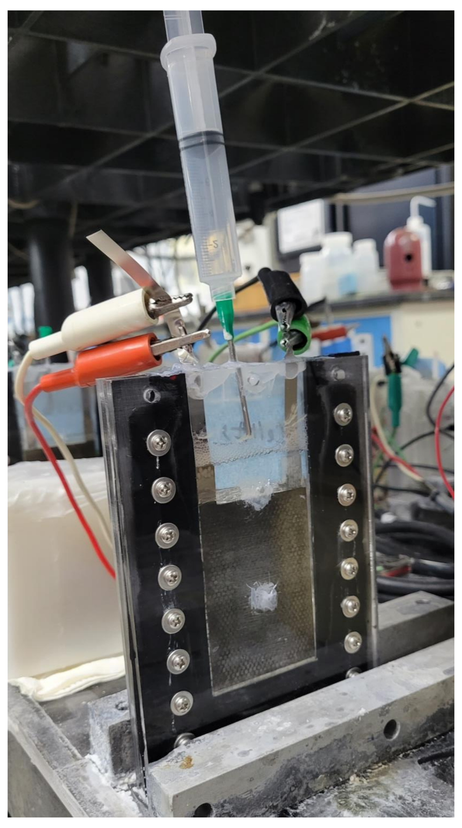
Material	Density (g/cm^3)	Volume Expansion vs. pure Zn
Metallic Zinc	7.133	1
Zinc Oxide	5.61	1.27
Calcium Zincate	2.59	2.75



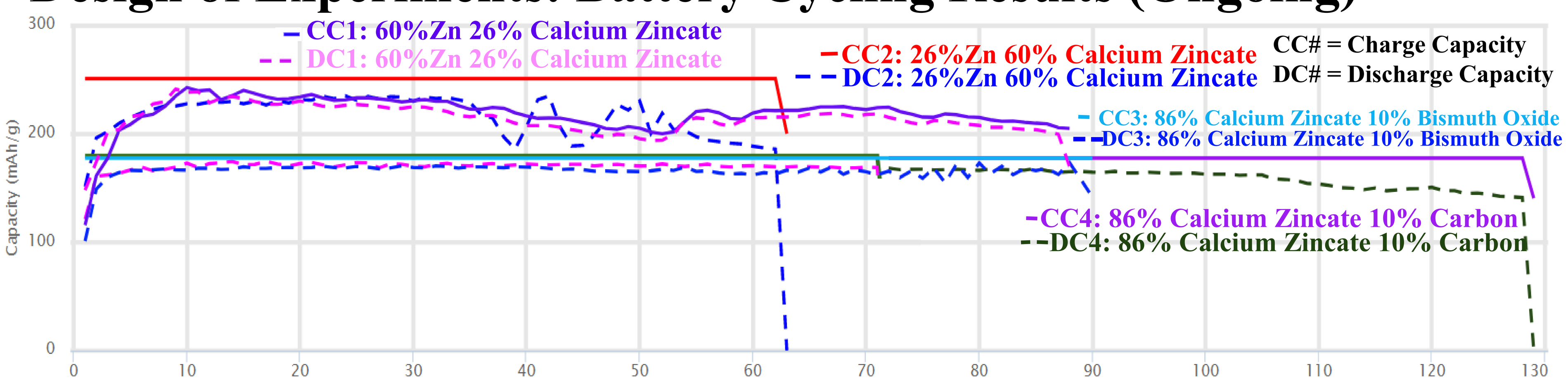
Design of Experiments: 2 x 3 in Anode vs SiNi Fabrication

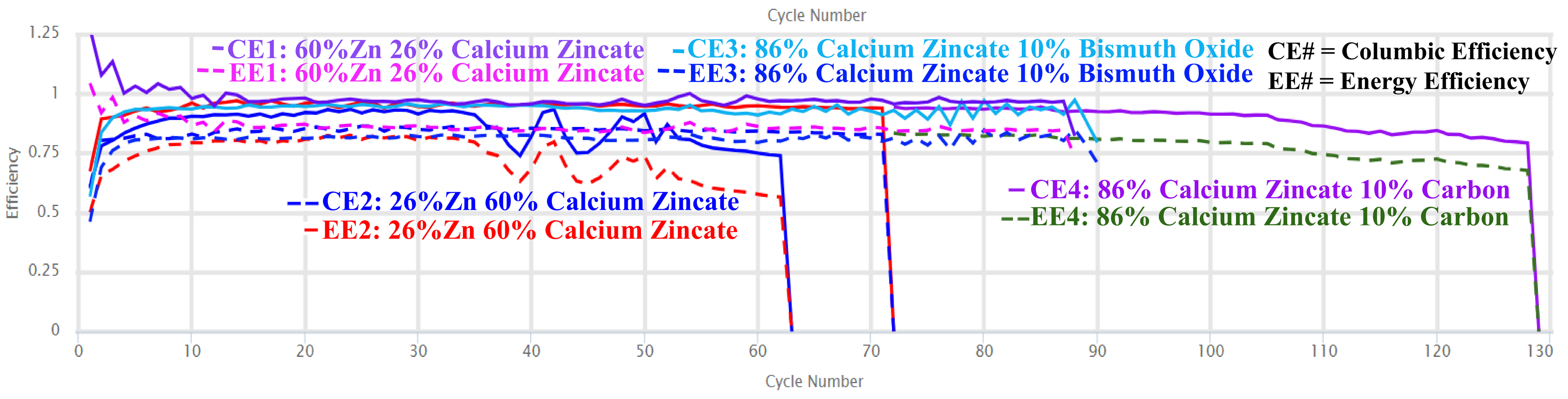






Design of Experiments: Battery Cycling Results (Ongoing)





Preliminary Conclusions/ Future Directions

- Various formulations of Calcium Zincate can be cycled with high 50% utilization of the active zinc material for more than 129+ ongoing cycles with greater than 80% capacity retention
- Understand the key factors during battery cycling at the nanoscale that led to the improved material utilization at high cycle life compared to metallic zinc
- Investigate hydrogen evolution reaction (HER) and possible additives to reduce zinc anode gassing
- Investigate calcium zincate anodes vs manganese dioxide (Zn-MnO_2) cells

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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