Investigation of Calcium Zincate ($Ca[Zn(OH)_3]_2 \cdot 2H_2O$) Cycling Performance for Rechargeable Alkaline Zinc Batteries

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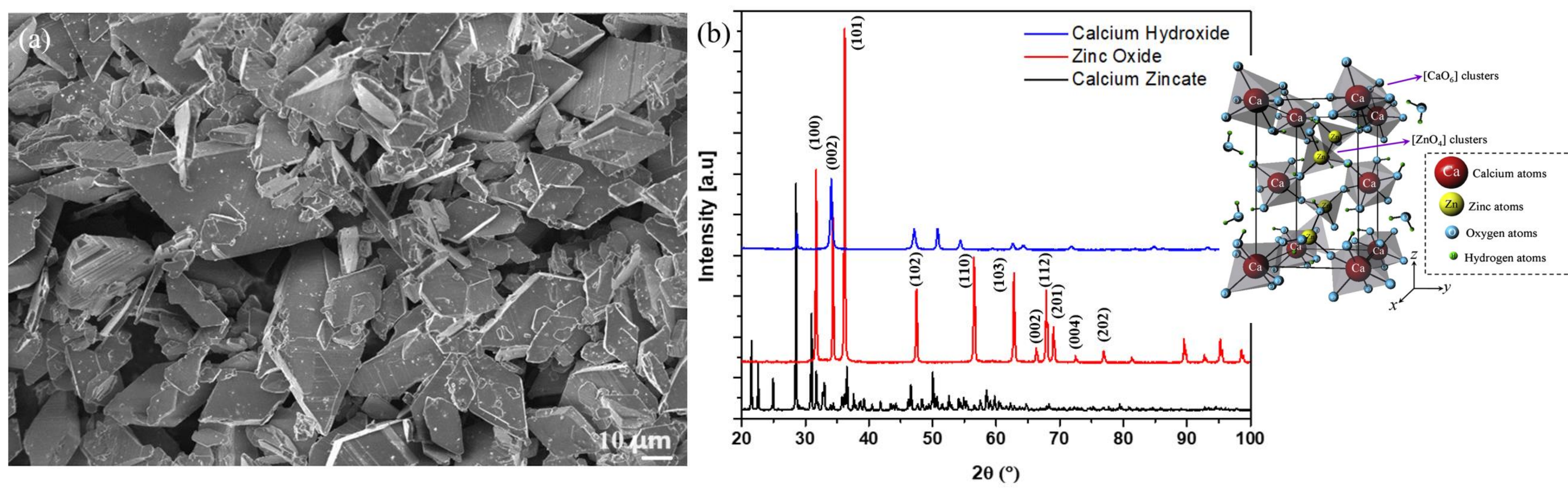
Objective: Investigate mechanism of Calcium Zincate and additives to improve performance

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 →

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

← Discharge

Rough Estimate on Raw Materials Cost at Scale*

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

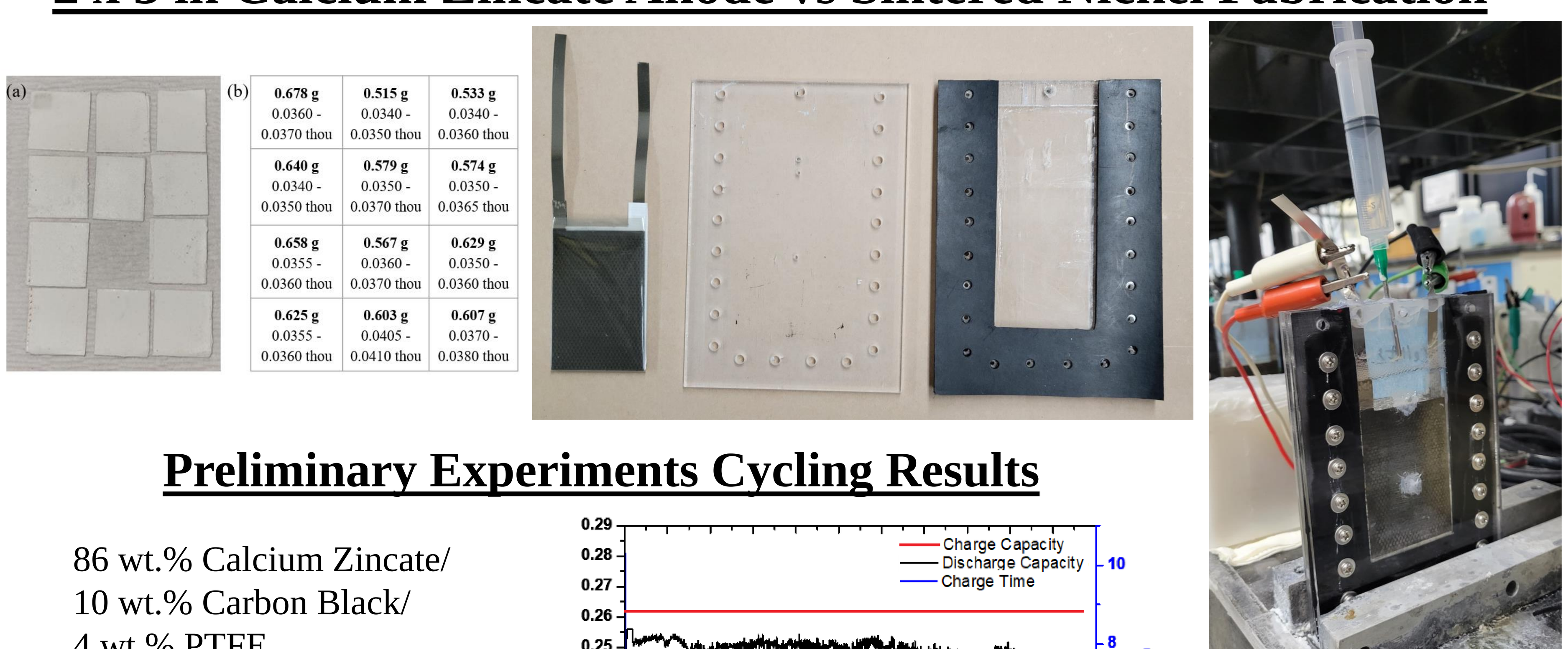
Zn ($/kg)	ZnO ($/kg)	Rough Estimate of Calcium Zincate based on starting materials ($/kg)	Bi_2O_3 ($/kg)	$Ca(OH)_2$ ($/kg)	PTFE Dispersion 60 wt.% Solids in water ($/kg)	25 wt.% KOH ($/kg)
4.06	1	1.71	8	0.3	9.43	0.95

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

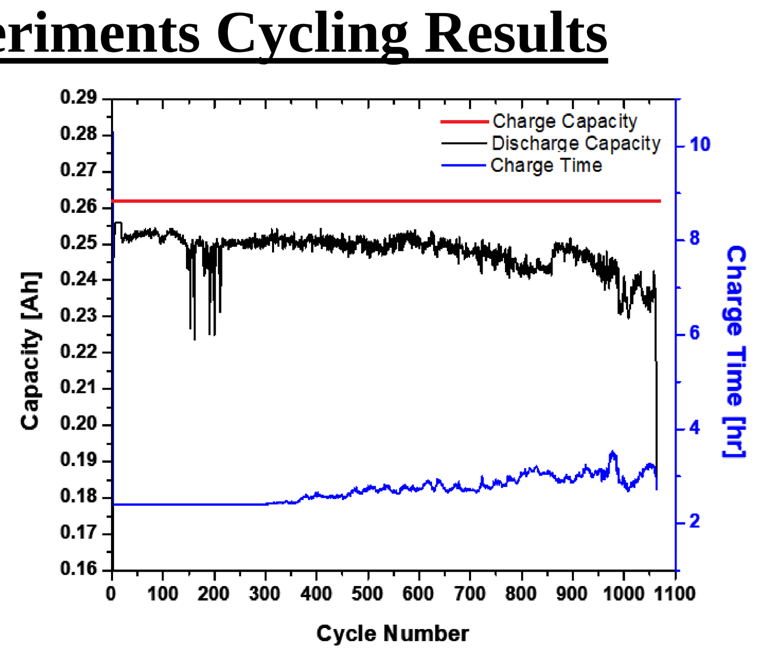
* Raw material cost information was all obtained publicly from multiple vendors on www.Alibaba.com. Calcium zincate price estimated assuming 20% KOH can be recycled at 90% of the fresh KOH cost, DI water treatment cost $0.5/L, additional cost of factory labor, energy, and equipment is 15% on top of the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

2 x 3 in Calcium Zincate Anode vs Sintered Nickel Fabrication



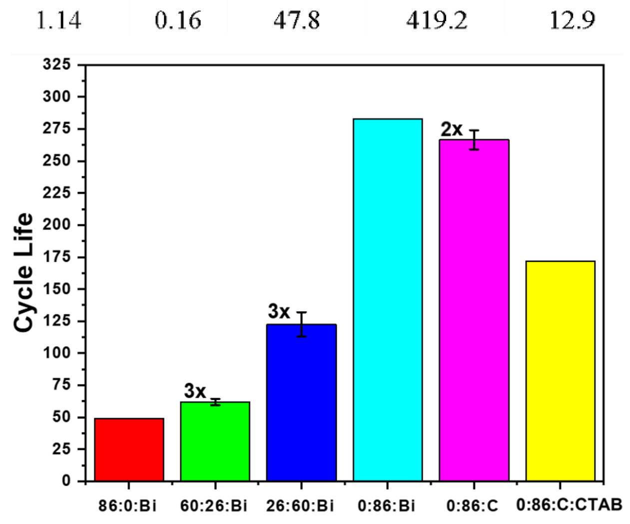
Preliminary Experiments Cycling Results

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



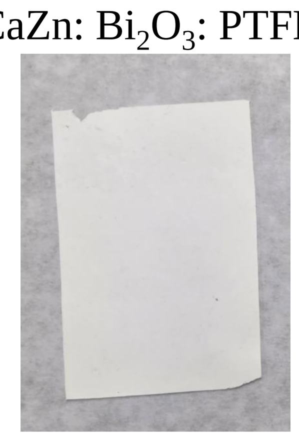
Name Zn:CaZn wt. % then additives	Total mass (g)	Zn metal (g)	CaZn (g)	Anode Composition (remaining balance PTFE binder) (wt.%)	Theoretical Capacity (Ah)	Theoretical Specific Capacity (mAh/g)	Anode Pressed Thickness ±10% (mm)	Anode Mass Loading (g/cm^2)	Theoretical Areal Capacity (mAh/cm^2)	Theoretical Volumetric Capacity (mAh/cm^3)	Anode Material Slurry Cost ($/kg)
96:0:none	2.35	2.26	0	96% Zn	1.85	787.2	-	0.06	47.8	-	10.1
86:0:Bi	2.63	2.26	0	86% Zn, 10% Bi_2O_3	1.85	703.4	0.23	0.07	47.8	2077.9	12.3
60:26:Bi	3.18	1.91	0.83	60% Zn, 26% CaZn, 10% Bi_2O_3	1.85	581.8	0.41	0.08	47.8	1165.7	12.9
26:60:Bi	4.39	1.14	2.63	26% Zn, 60% CaZn, 10% Bi_2O_3	1.85	421.4	0.68	0.11	47.8	702.8	14.3
0:86:Bi	6.20	0	5.33	86% CaZn, 10% Bi_2O_3	1.85	298.4	0.84	0.16	47.8	568.9	16.4
0:86:C	6.20	0	5.33	86% CaZn, 10% Carbon	1.85	298.4	1.06	0.16	47.8	450.9	13.3
0:86:C:CTAB	6.20	0	5.33	86% CaZn, 9% Carbon, 2% CTAB	1.85	298.4	1.14	0.16	47.8	419.2	12.9

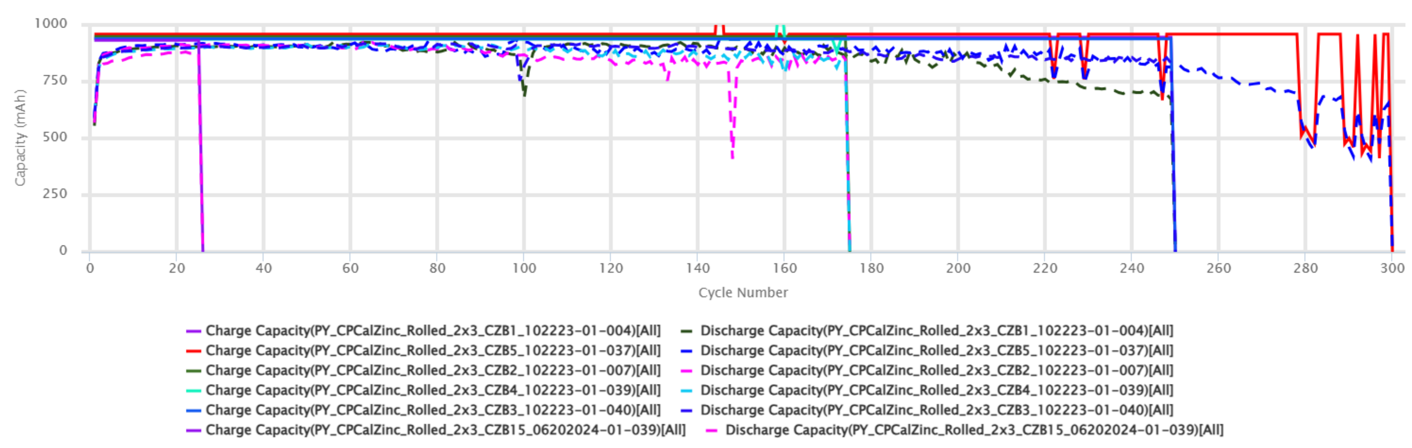
- Comparing Zn anodes with CaZn anodes both with Bi_2O_3 under the same conditions there is approximately 25% increase in the raw materials cost, but a five time increase in cycle life.
- When considering the cost of the anodes per cycle life, there is a noticeable decrease of cost from ~$0.016 per kg per discharge kWh per cycle (pure Zn) to ~ $0.012 per cycle (pure CaZn) equating to a ~25% reduction in cost per cycle.



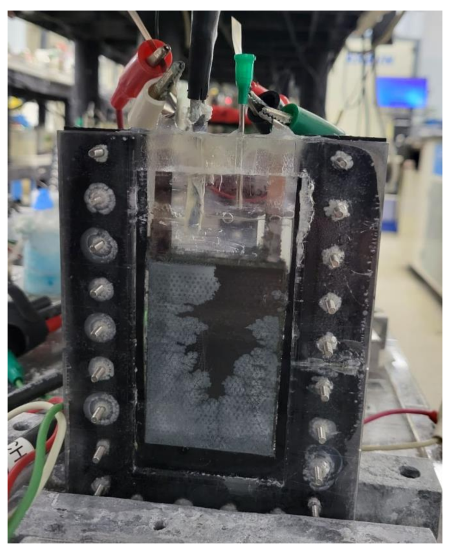
50% Zinc Utilization in 20% KOH - Battery Cycling Results

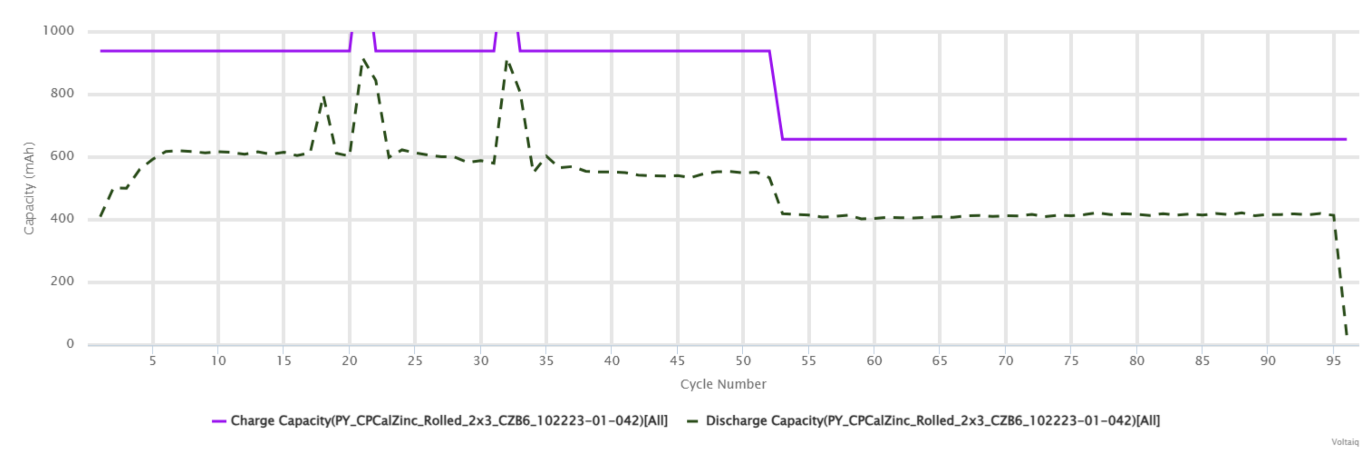
86:10:4
CaZn: Bi_2O_3: PTFE



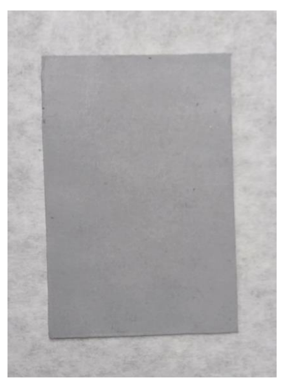


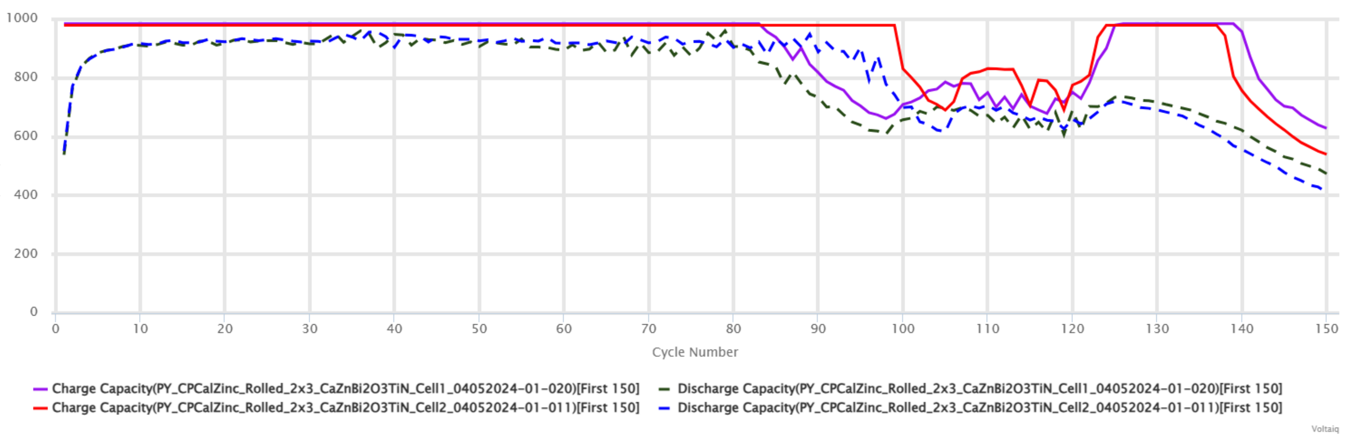
Cell Name	# Cycle	% Zn Utilization
CZB1	100	0% "Discharged"
CZB3	101	50% "Charged"
CZB2	175	0%"Discharged"
CZB4	176	50% "Charged"
CZB5	300	0% "Discharged"
CZB15	301	50% "Charged"



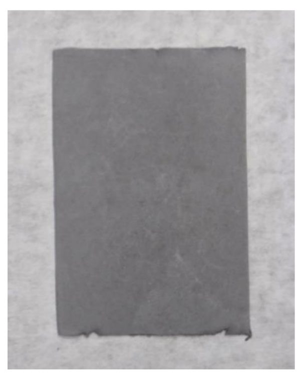


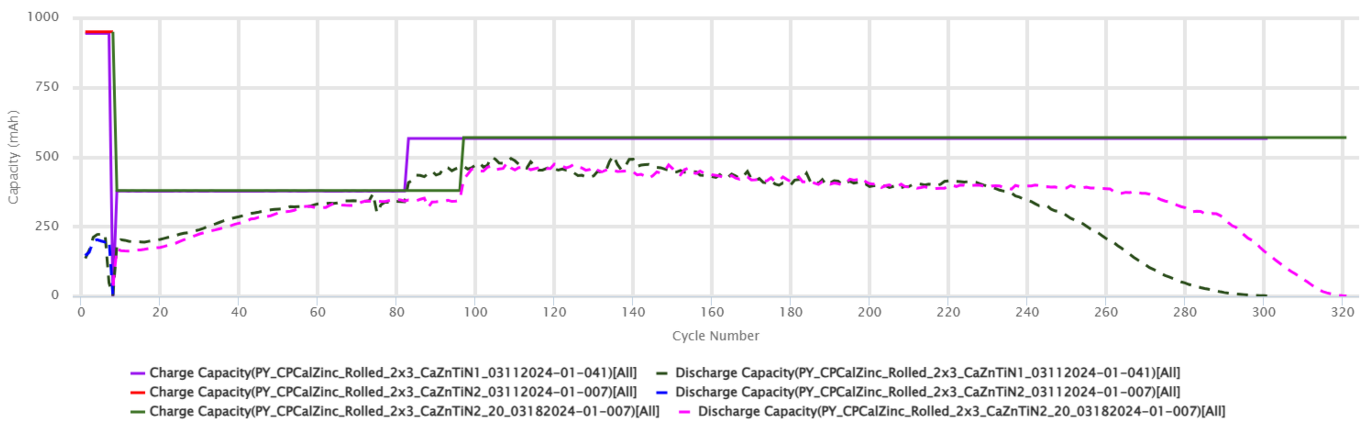
86:5:5:4
CaZn: Bi_2O_3 :TiN: PTFE





86:10:4
CaZn: TiN: PTFE





Preliminary Conclusions/ Future Directions

- The addition of Titanium Nitride (TiN) is investigated as an additive for Calcium Zincate anodes showing poor performance on its own and requires bismuth oxide to cycle properly
- Long durational discharge is investigated but shows poor ~60% coulombic and energy efficiency
- Will investigate Calcium Zincate nanostructure before, during, and after cell failure to understand the mechanism of CaZn cycling behaviors
- Will investigate hydrogen evolution reaction (HER) and possible additives to reduce zinc anode gassing

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