Electronic Supplementary Material (ESI) for Energy Advances.

Supplemental Information

Performance and Failure Mechanisms of Alkaline Zinc Anodes with Addition of Calcium Zincate ($Ca[Zn(OH)_3]_2 \cdot 2H_2O$) Under Industrially Relevant Conditions

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Supplemental Figures

Table S1 a) Bill of materials (BOM) for different materials needed for calcium zincate (CaZn) based anodes, rough estimates of cost ($/kg) at scale from publicly available seller information on Alibaba.com in 2023 **b**) Rough estimate of theoretical cost of CaZn based on starting materials.

(a) 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

(b) 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

Table S2: Summary of all cycled anode compositions types, names, and cycles until 70% capacity retention for each anode with repeats.

Cell #	Name Zn:CaZn wt. % then additives	Anode Composition (remaining balance PTFE binder) (wt.%)	Cell Names	20% Zn Utilization Cycle life (70% Capacity Retention)
1	86:0:C	86% Zn, 10% Acetylene Carbon Black	PY_CalZinc_Carbon_Repeat6_2 x3_052722-01-035	1062

Cell #	Name Zn:CaZn wt. % then additives	Anode Composition (remaining balance PTFE binder) (wt.%)	Cell Names	50% Zn Utilization Cycle life (70% Capacity Retention)	Total Charged Energy (Wh/cycle) (70% Capacity Retention)	Total Discharged Energy (Wh/cycle) (70% Capacity Retention)
2	86:0:Bi	86% Zn, 10% Bi_2O_3	PY_Zn_Bi2O3_2x3_Cell_S3-01-035	49	0.737	0.579
3	60:26:Bi	60% Zn, 26% CaZn, 10% Bi_2O_3	PY_CalZinc_Zn_Bi2O3_2x3_Cell _1D_102122-01-037	31	0.821	0.645
4			PY_CalZinc_Zn_Bi2O3_2x3_Cell _12_121722-01-033	60	1.682	1.382
5			PY_CalZinc_Zn_Bi2O3_2x3_Cell _1C_102122-01-039	61	1.610	1.292
6	26:60:Bi	26% Zn, 60% CaZn, 10% Bi_2O_3	PY_CalZinc_Zn_Bi2O3_2x3_Cell _2A_111322-01-036	65	1.741	1.150
7			PY_CalZinc_Zn_Bi2O3_2x3_Cell _3-01-041	132	1.823	1.081
8			PY_CalZinc_Zn_Bi2O3_2x3_Cell _3A_cont_011223-01-099	113	1.833	0.931
9			PY_CalZinc_Zn_Bi2O3_2x3_Cell _4A_01052023-01-039	270	1.767	1.255
10	0:86:Bi	86% CaZn, 10% Bi_2O_3	PY_CalZinc_Zn_Bi2O3_2x3_Test 7_091922-01-042	283	1.805	1.177
11	0:86:C	86% CaZn, 10% Acetylene Carbon Black	PY_CalZinc_Zn_Bi2O3_2x3_Cell _8-01-038	274	1.786	1.255
12			PY_CalZinc_Zn_Bi2O3_2x3_Cell _9_1-01-040	259	1.570	0.952
13	0:86:C:CTAB	86% CaZn, 9% Acetylene Carbon Black, 2% CTAB	PY_CalZinc_Carbon_CTAB_2x3_ Cell_9A-01-004	172	1.784	1.224

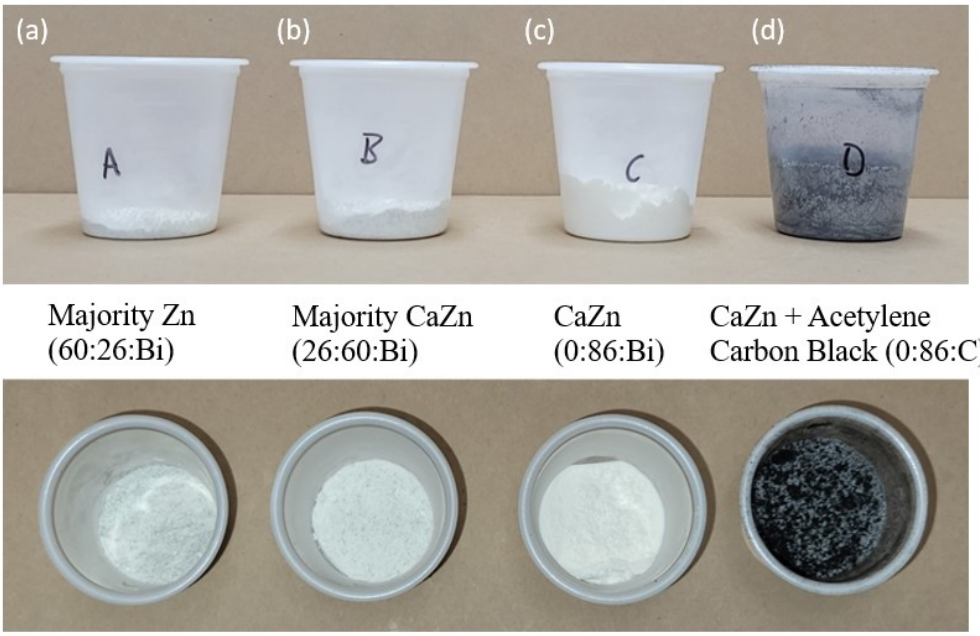


Figure S1: Optical image of dry powder without binders of the four common cell formulations (a) majority Zn (60:26:Bi), (b) majority CaZn (26:60:Bi), (c) pure CaZn (0:86:Bi), and (d) pure CaZn + acetylene carbon black (0:86:C)

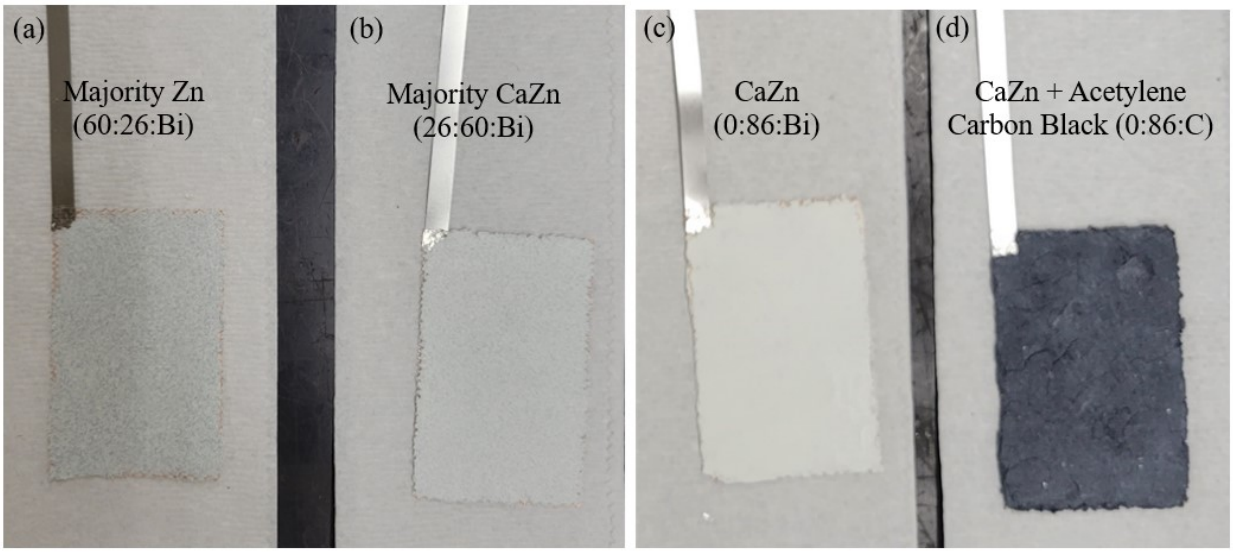


Figure S2: Images of (a) cell formulation #1 (majority Zn (60:26:Bi)), (b) cell formulation #2 (majority CaZn (26:60:Bi)), (c) cell formulation #3 (pure CaZn (0:86:Bi)), and cell formulation #4 (pure CaZn (0:86:C))

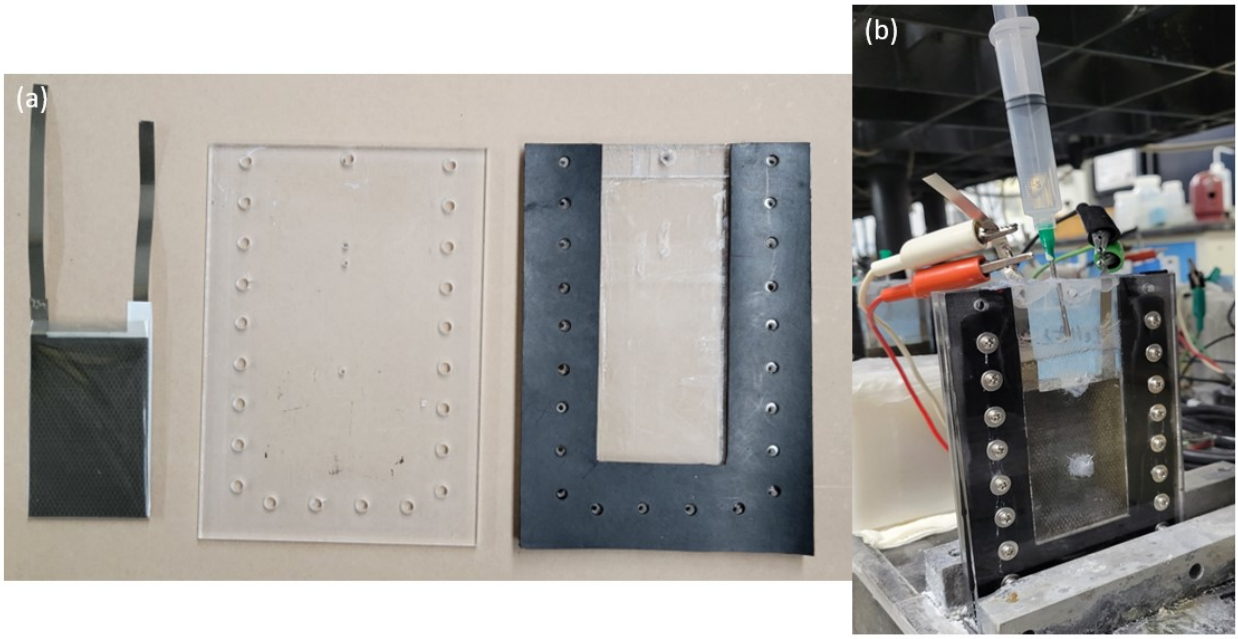


Figure S3: Images showing (a) anode and cathode battery pack wrapped with separators (b) two custom cut PMMA plexiglass sheets and buna rubber gasket with screw holes, and (c) fully assembled and sealed battery.

(a)

(b)

0.387 g 0.0120 - 0.0160 thou	**0.314 g** 0.0110 - 0.0115 thou	**0.287 g** 0.0100 - 0.0105 thou
0.348 g 0.0110 - 0.0115 thou	**0.347 g** 0.0110 - 0.0115 thou	**0.347 g** 0.0105 - 0.0110 thou
0.360 g 0.0110 - 0.0115 thou	**0.358 g** 0.0110 - 0.0115 thou	**0.364 g** 0.0105 - 0.0110 thou
0.325 g 0.0110 - 0.0115 thou	**0.337 g** 0.0105 - 0.0110 thou	**0.345g** 0.0100 - 0.0105 thou

Figure S4: a) Optical image of freshly rolled, pressed, and dissected anode cell formulation #1 (60 wt.% Zn, 26 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE) B) Table showing the weight and thickness of the samples.

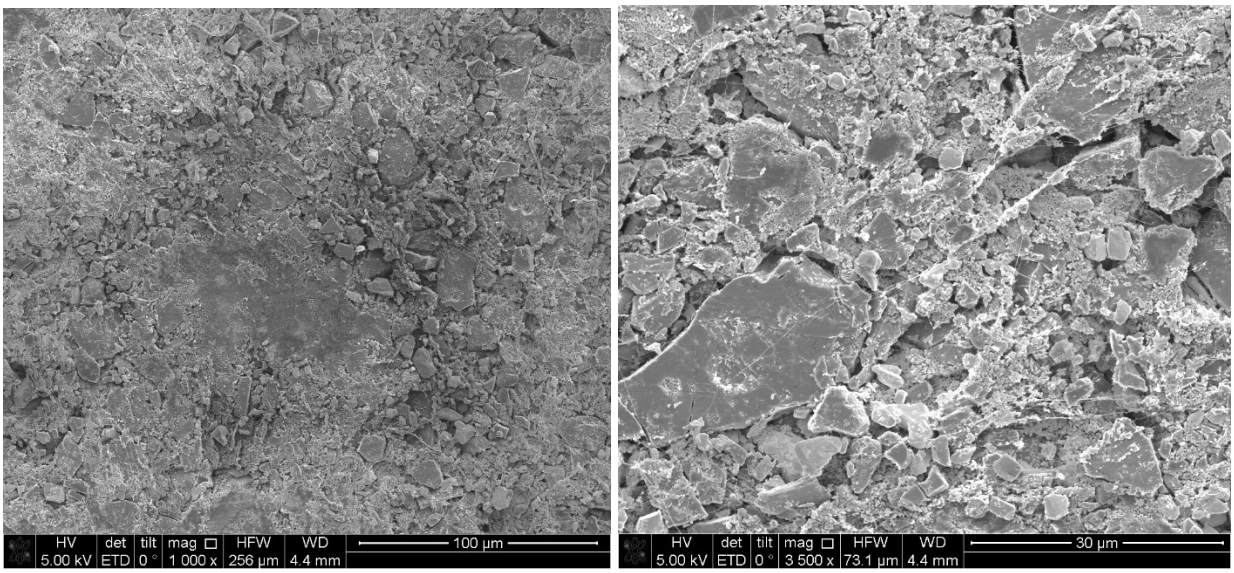


Figure S5: SEM image of freshly rolled and pressed anode cell formulation #1 (60 wt.% Zn, 26 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

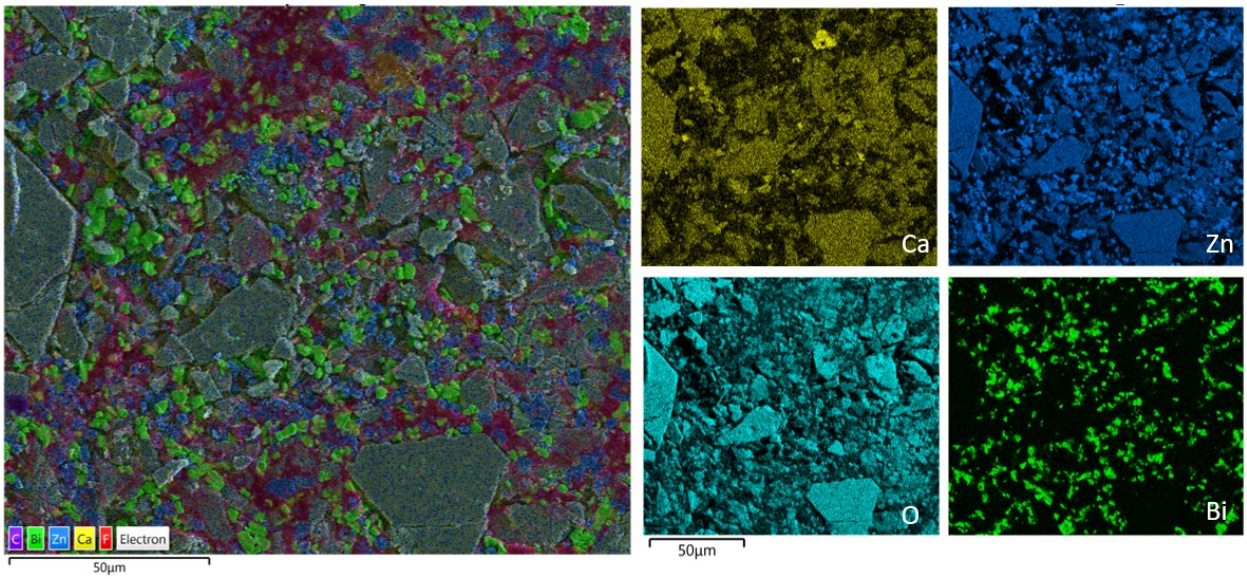


Figure S6: Top-down SEM image of freshly rolled and pressed anode cell formulation #1 (60 wt.% Zinc, 26 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

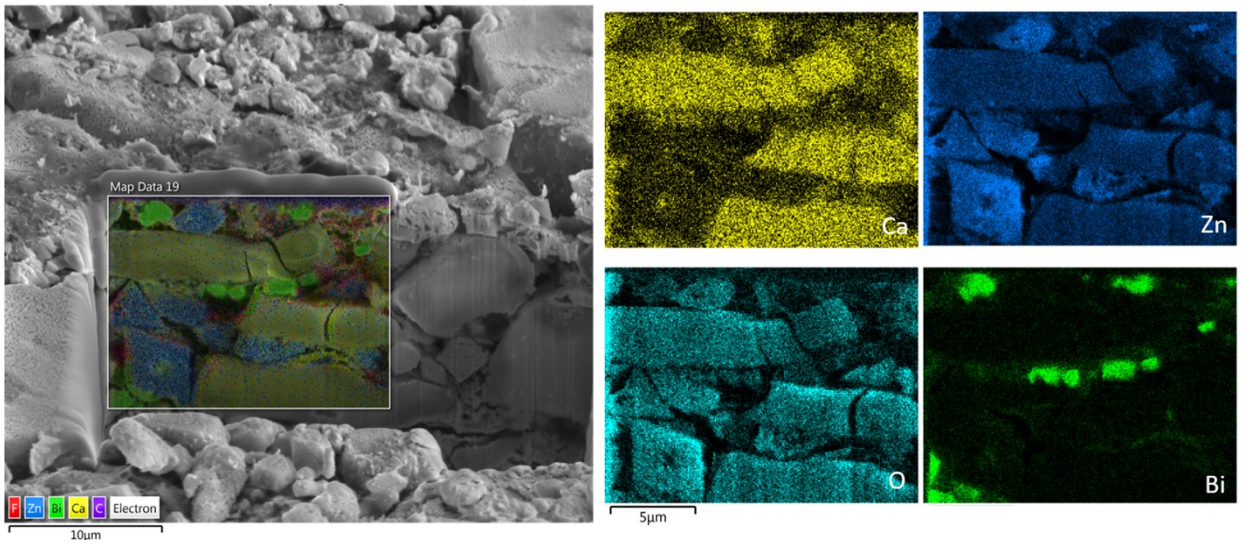


Figure S7: SEM-FIB EDS mapping image of freshly rolled and pressed anode cell formulation #1 (60 wt.% Zinc, 26 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

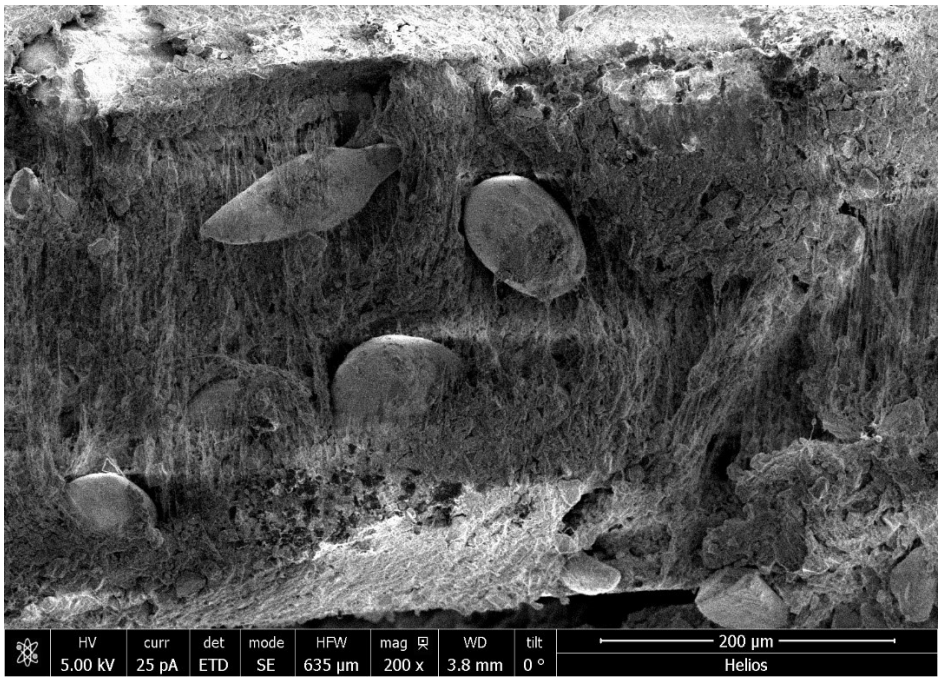


Figure S8: Cross-sectional SEM image of freshly rolled and pressed anode cell formulation #1 (60 wt.% Zinc, 26 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

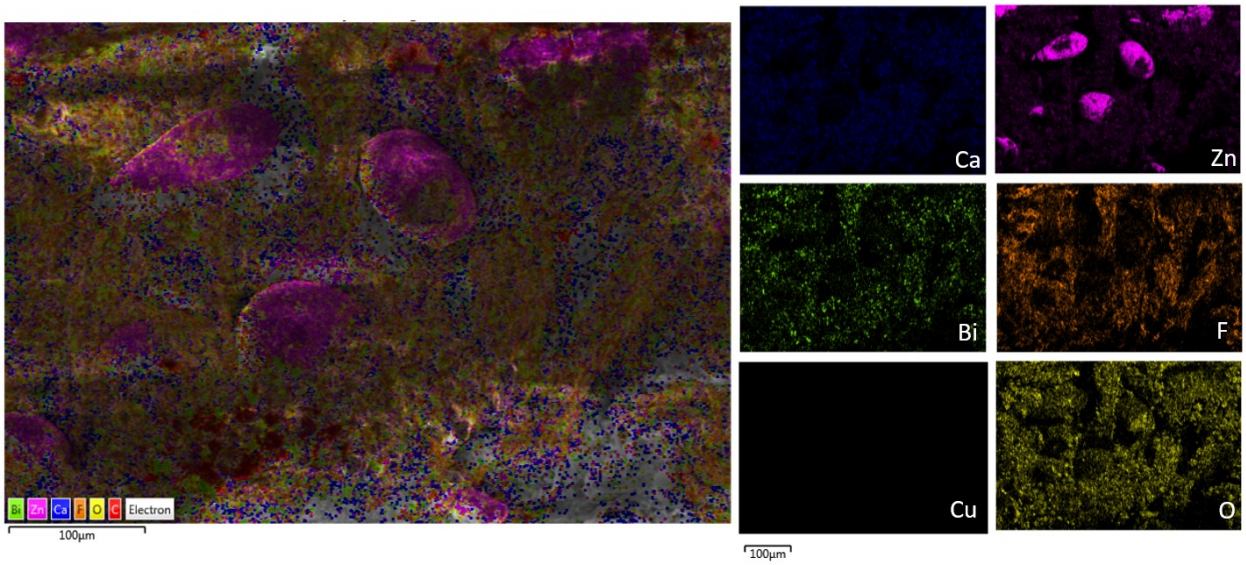
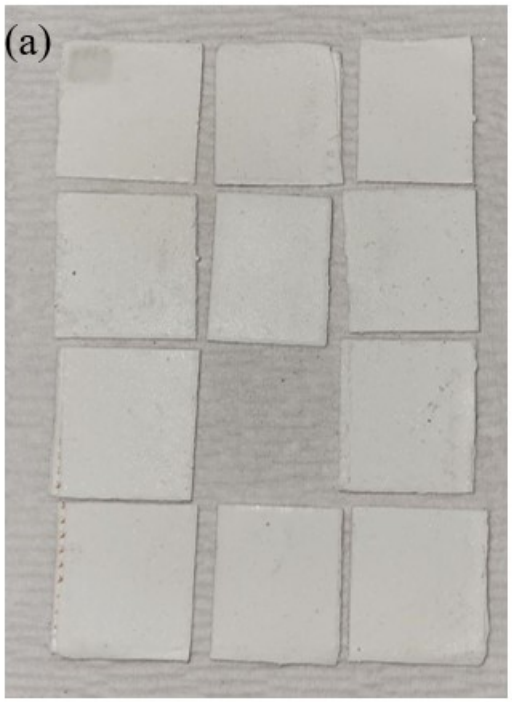


Figure S9 Cross sectional SEM- EDS mapping of cell formulation #1 (60 wt.% Zinc, 26 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE) showing elemental mapping of the anode before cycling.



(b)

0.678 g 0.0360 - 0.0370 thou	**0.515 g** 0.0340 - 0.0350 thou	**0.533 g** 0.0340 - 0.0360 thou
0.640 g 0.0340 - 0.0350 thou	**0.579 g** 0.0350 - 0.0370 thou	**0.574 g** 0.0350 - 0.0365 thou
0.658 g 0.0355 - 0.0360 thou	**0.567 g** 0.0360 - 0.0370 thou	**0.629 g** 0.0350 - 0.0360 thou
0.625 g 0.0355 - 0.0360 thou	**0.603 g** 0.0405 - 0.0410 thou	**0.607 g** 0.0370 - 0.0380 thou

Figure S10: a) Image of freshly rolled and pressed anode cell formulation #3 (86 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE) dissected for analysis b) Table showing the weight and thickness range of the samples.

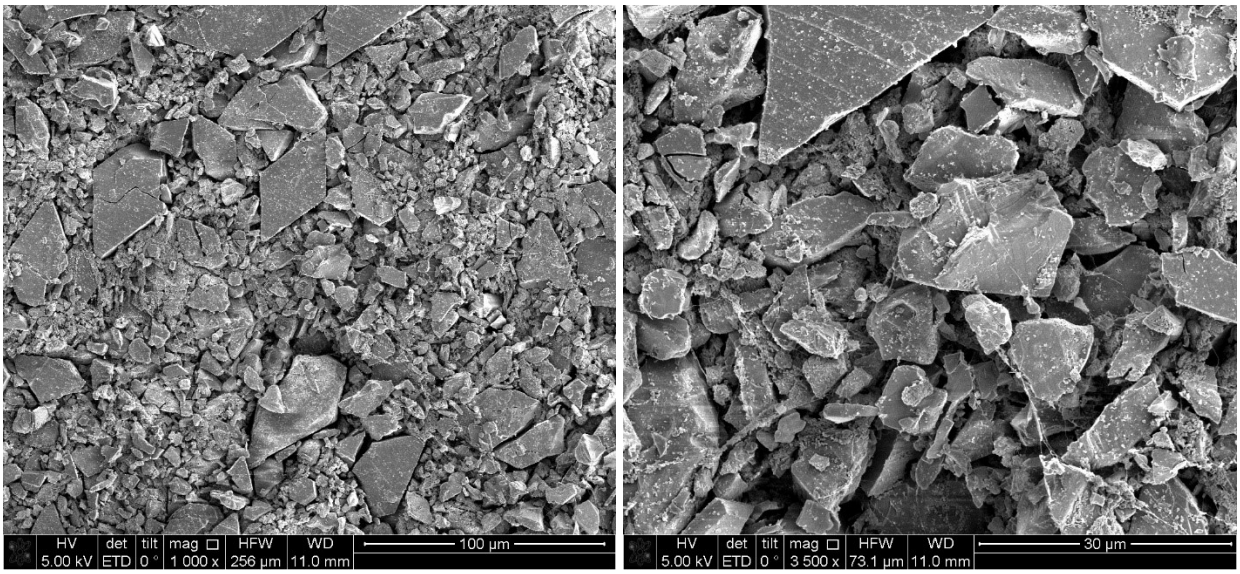


Figure S11: Top-down SEM images of freshly rolled and pressed anode cell formulation #3 (86 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

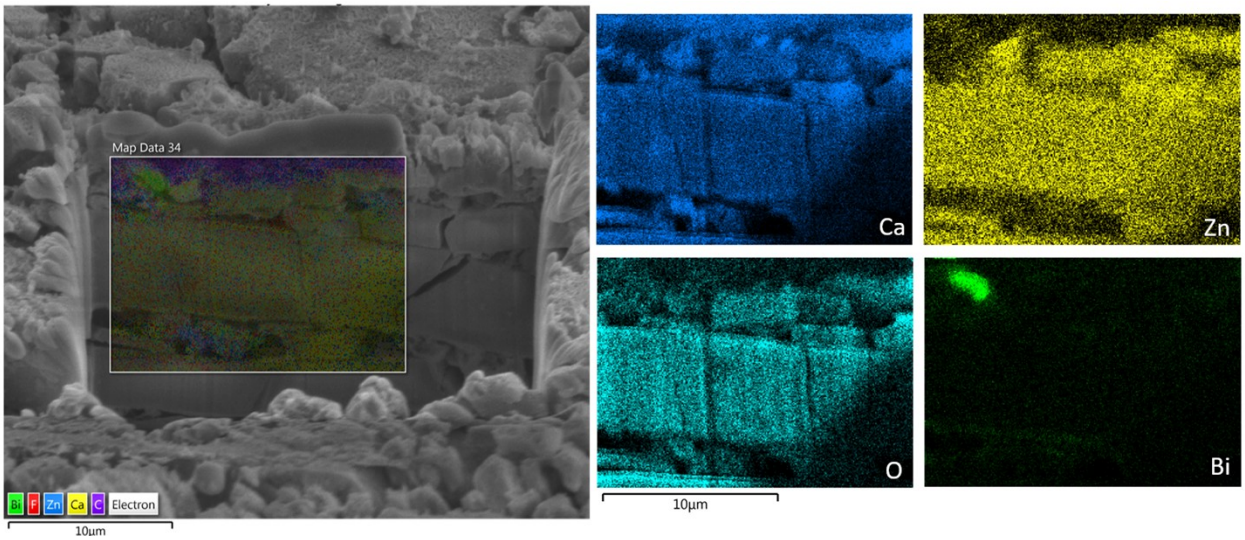


Figure S12: SEM-FIB EDS image of freshly rolled and pressed anode cell formulation #3 (86 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

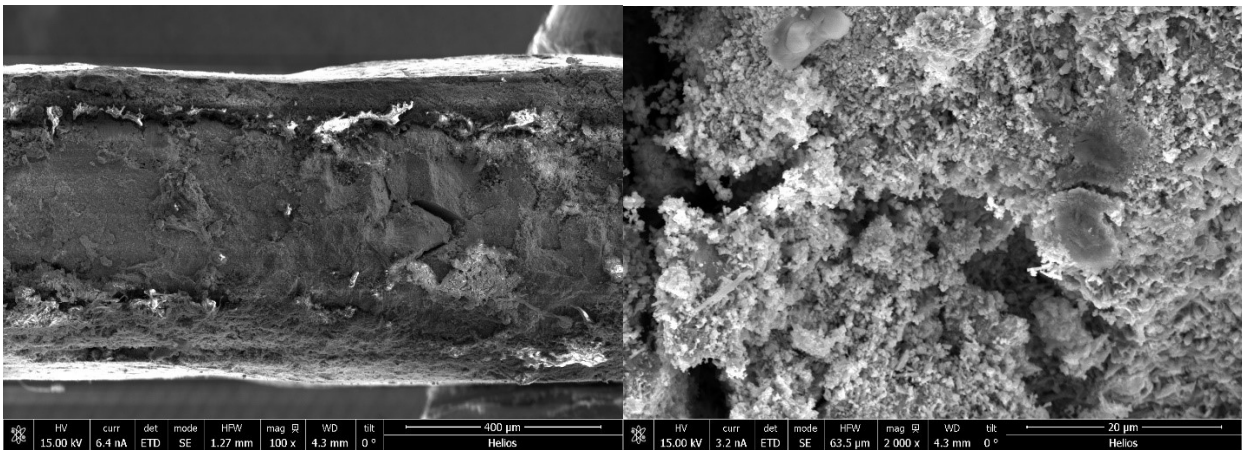


Figure S13: Cross-sectional SEM of cycled Cell #12–- anode cell formulation #1 majority Zn vs SiNi cathodes (60 wt.% Zn, 26 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

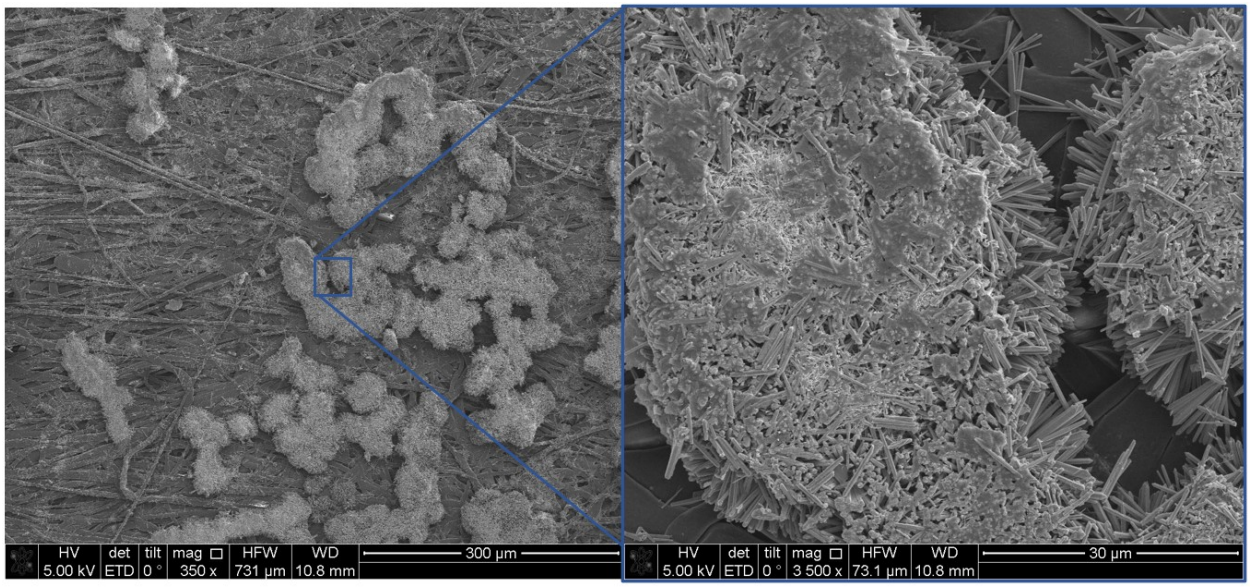


Figure S14: Top-down SEM image of failed cycled Cell #12–- anode cell formulation #1 majority Zn vs SiNi cathodes (60 wt.% Zn, 26 wt.% CaZn 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

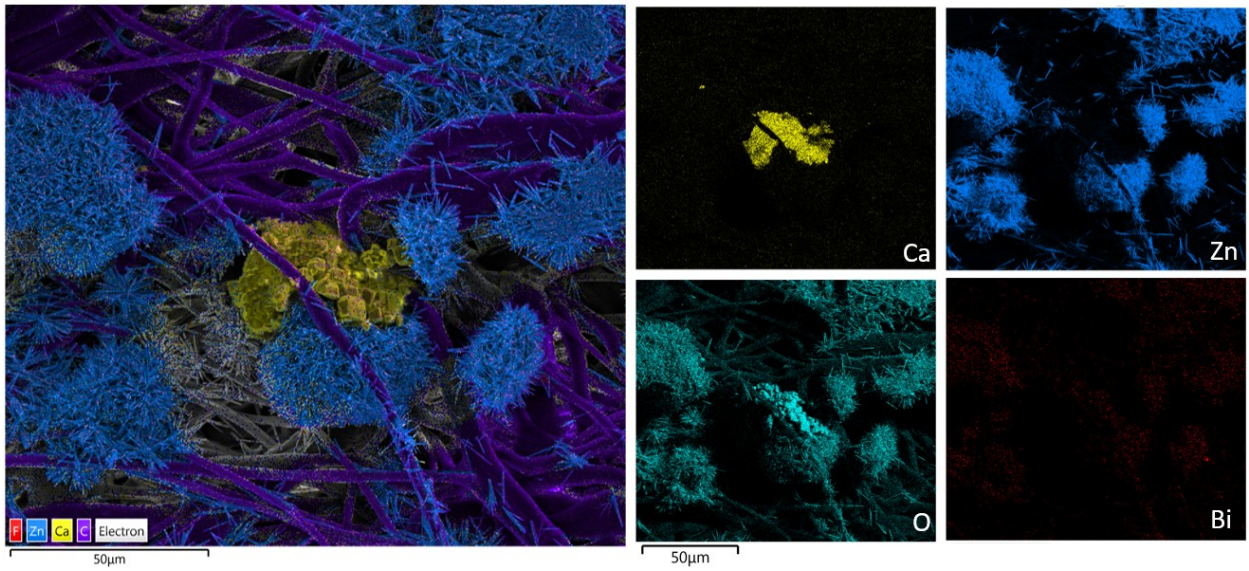


Figure S15: SEM-EDS mapping of cycled Cell #12 – anode cell formulation #1 majority Zn vs SiNi cathodes (60 wt.% Zn, 26 wt.% CaZn 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

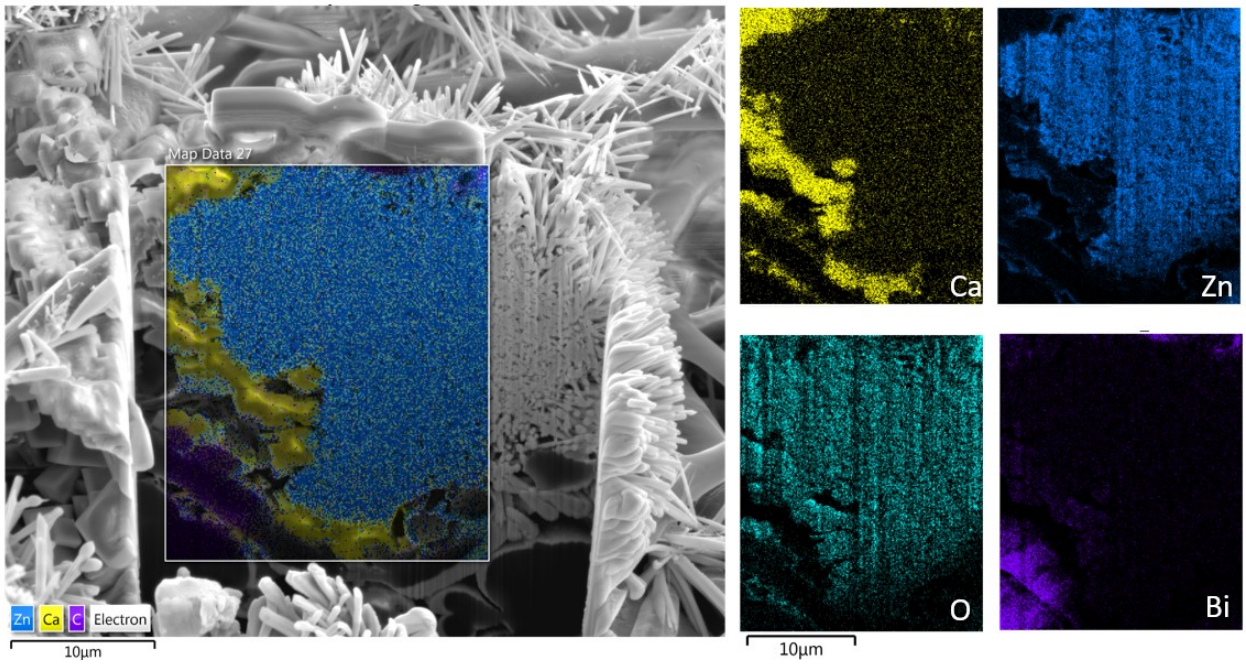


Figure S16: A) Image of cycled Cell #12 – anode cell formulation #1 majority Zn vs SiNi cathodes (60 wt.% Zn, 26 wt.% CaZn 10 wt.% Bi_2O_3, and 4 wt.% PTFE

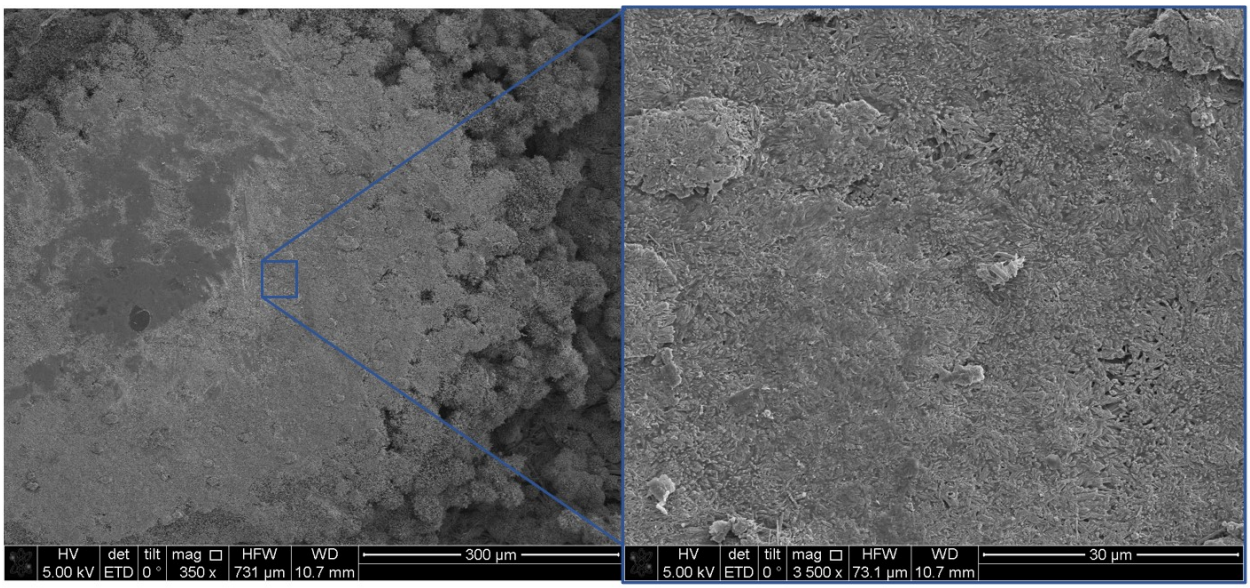


Figure S17: SEM image of cycled Cell #12 – anode cell formulation #1 majority Zn vs SiNi cathodes (60 wt.% Zn, 26 wt.% CaZn 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

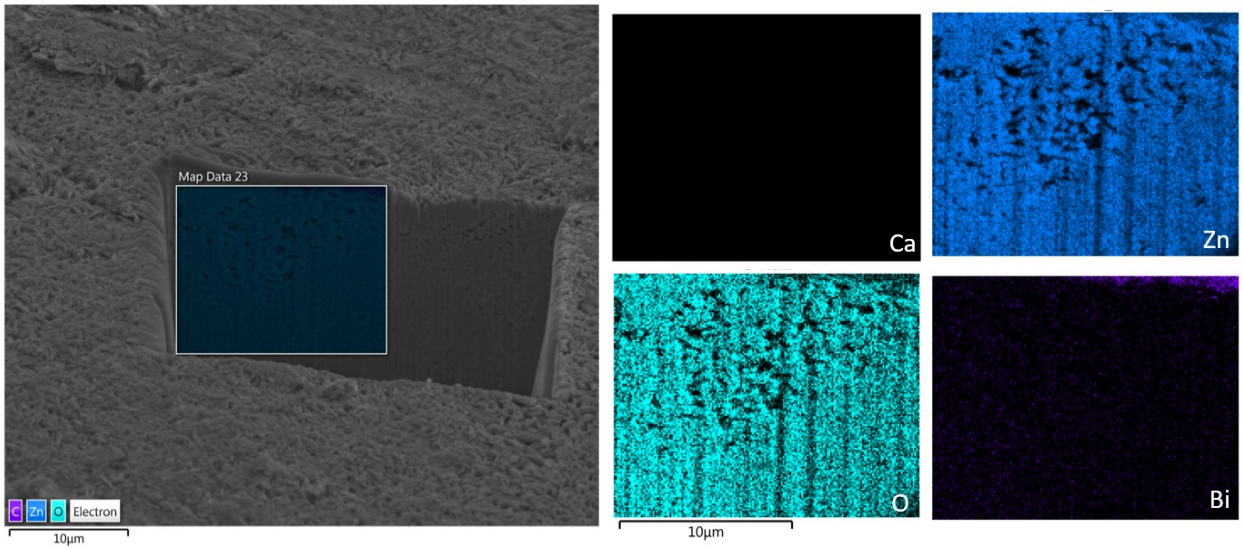


Figure S18: SEM-EDS mapping of cycled Cell #12 – anode cell formulation #1 majority Zn vs SiNi cathodes (60 wt.% Zn, 26 wt.% CaZn 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

(a)

(b)

0.31 g 0.0240 - 0.0250 thou	**0.34 g** 0.0295 - 0.0310 thou	**0.21 g** 0.0230 - 0.0275 thou
0.37 g 0.0275 - 0.0300 thou	**0.82 g** 0.0290 - 0.0320 thou	**0.34 g** 0.0280 - 0.0310 thou
0.36 g 0.0280 - 0.0315 thou	**1.01 g** 0.0290 - 0.0330 thou	**0.37 g** 0.0295 - 0.0340 thou
0.36 g 0.0250 - 0.0315 thou	**0.38 g** 0.0290 - 0.0350 thou	**0.38 g** 0.0240 - 0.0385 thou

Figure S19: A) Optical image of cycled Cell #1D – anode cell formulation #1 majority Zn vs MnO_2 cathodes (60 wt.% Zn, 26 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE) b) Table showing the weight and thickness range of the samples.

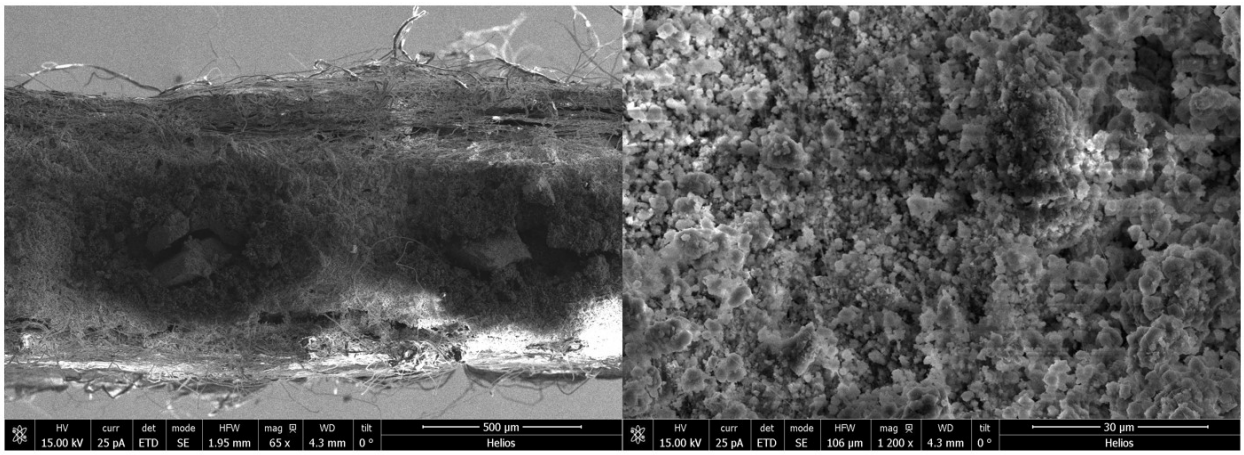


Figure S20: Cross-sectional SEM image of cycled Cell # 7–- anode cell formulation #3, (86 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

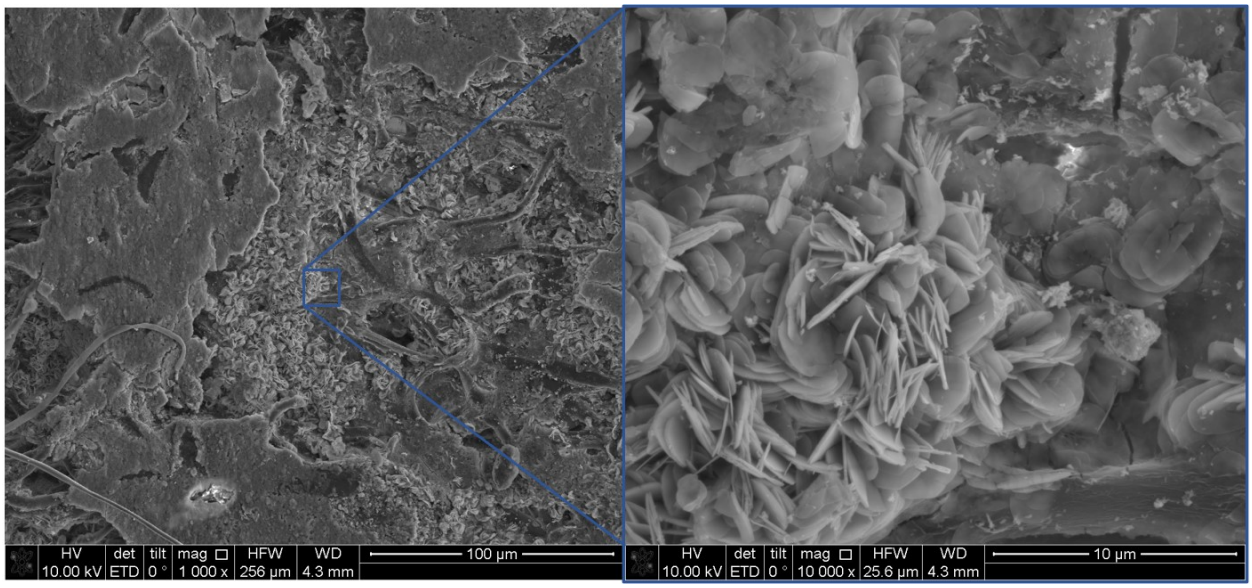


Figure S21: Top-down SEM image of cycled Cell # 7 – anode cell formulation #3, (86 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

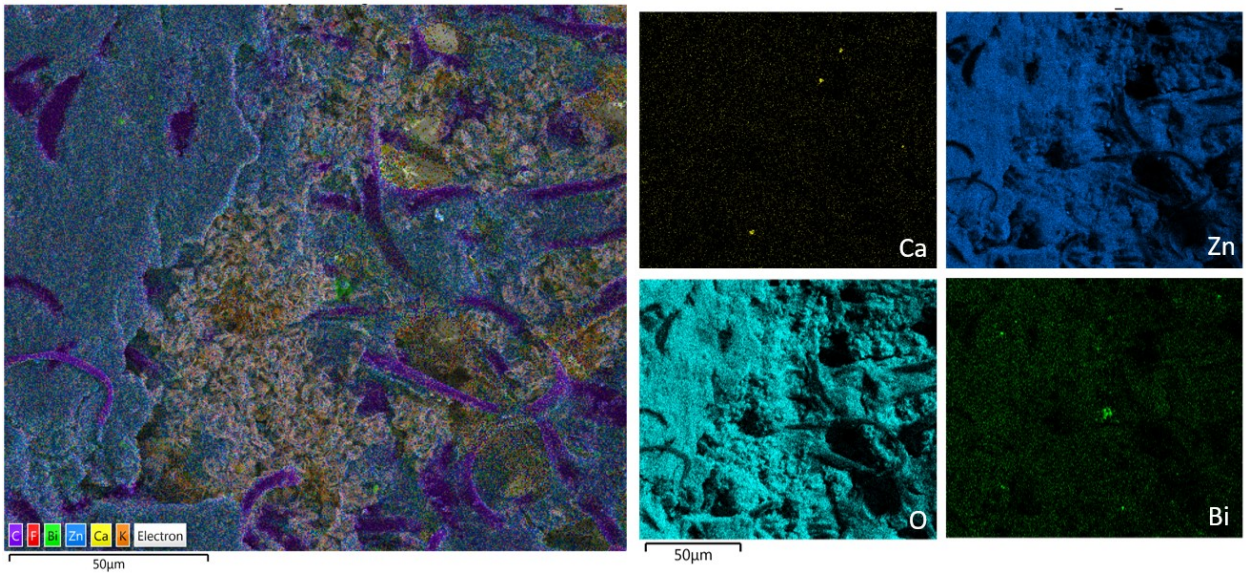


Figure S22: Top-down SEM-EDS image of cycled Cell # 7–- anode cell formulation #3, (86 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

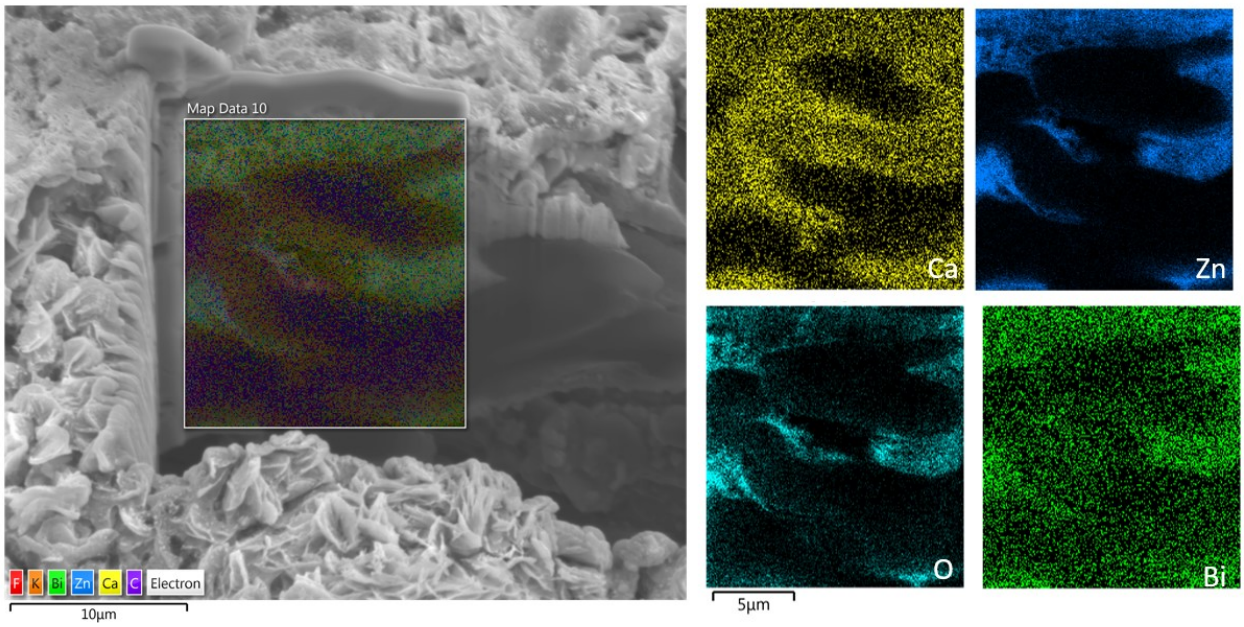


Figure S23: SEM-FIB EDS mapping of cycled Cell # 7–- anode cell formulation #3, (86 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

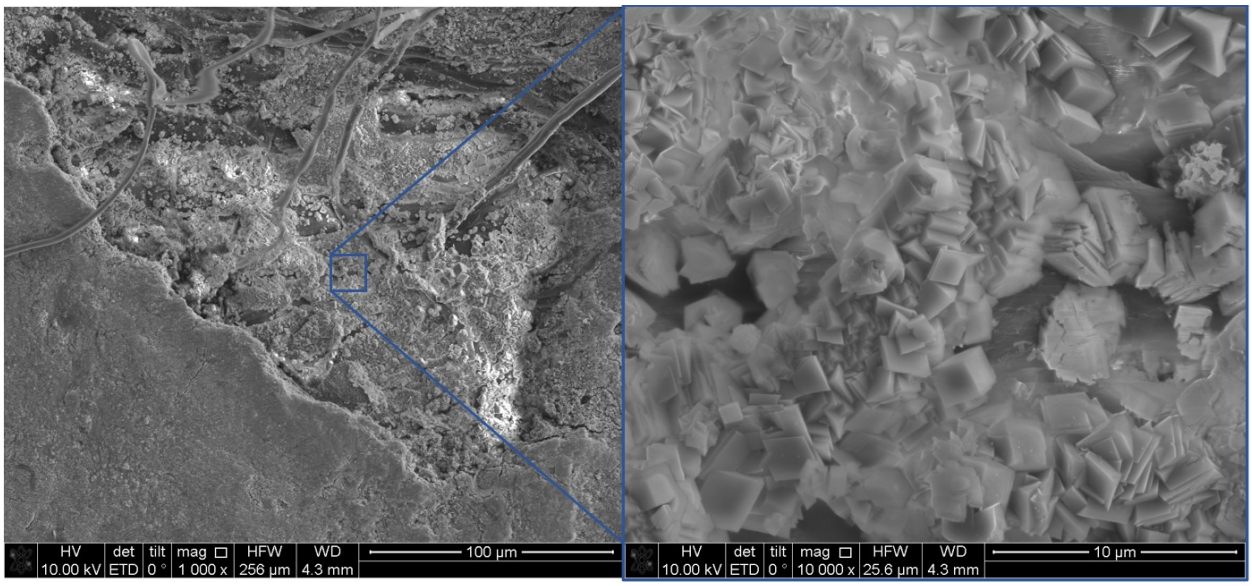


Figure S24: Top-down SEM image of cycled Cell # 7–- anode cell formulation #3, (86 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

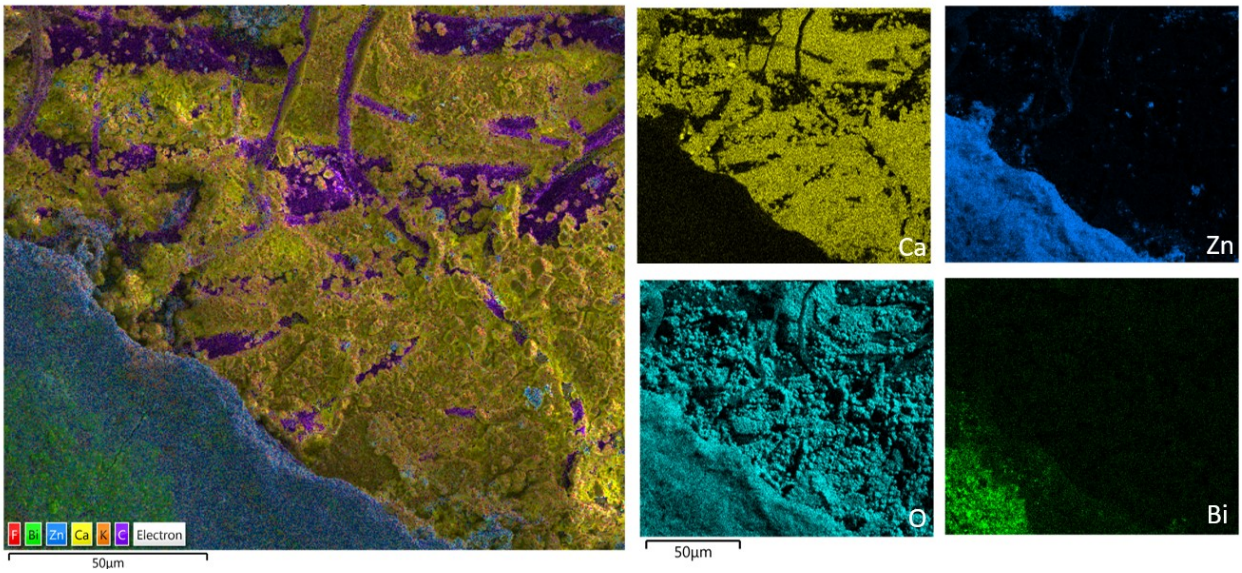


Figure S25: SEM-EDS mapping of cycled Cell # 7–- anode cell formulation #3, (86 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)

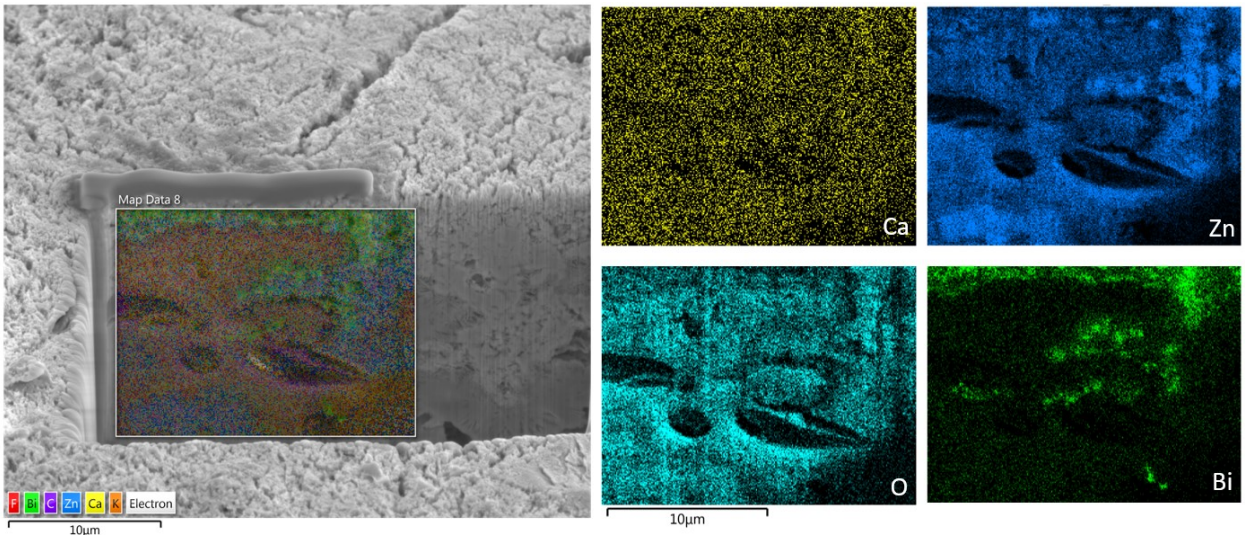


Figure S26: SEM-FIB EDS mapping of cycled Cell # 7– anode cell formulation #3, (86 wt.% CaZn, 10 wt.% Bi_2O_3, and 4 wt.% PTFE)