

Supporting Information

Statistical Approach to Design Zn Particle Size, Shape, and Crystallinity for Alkaline Batteries

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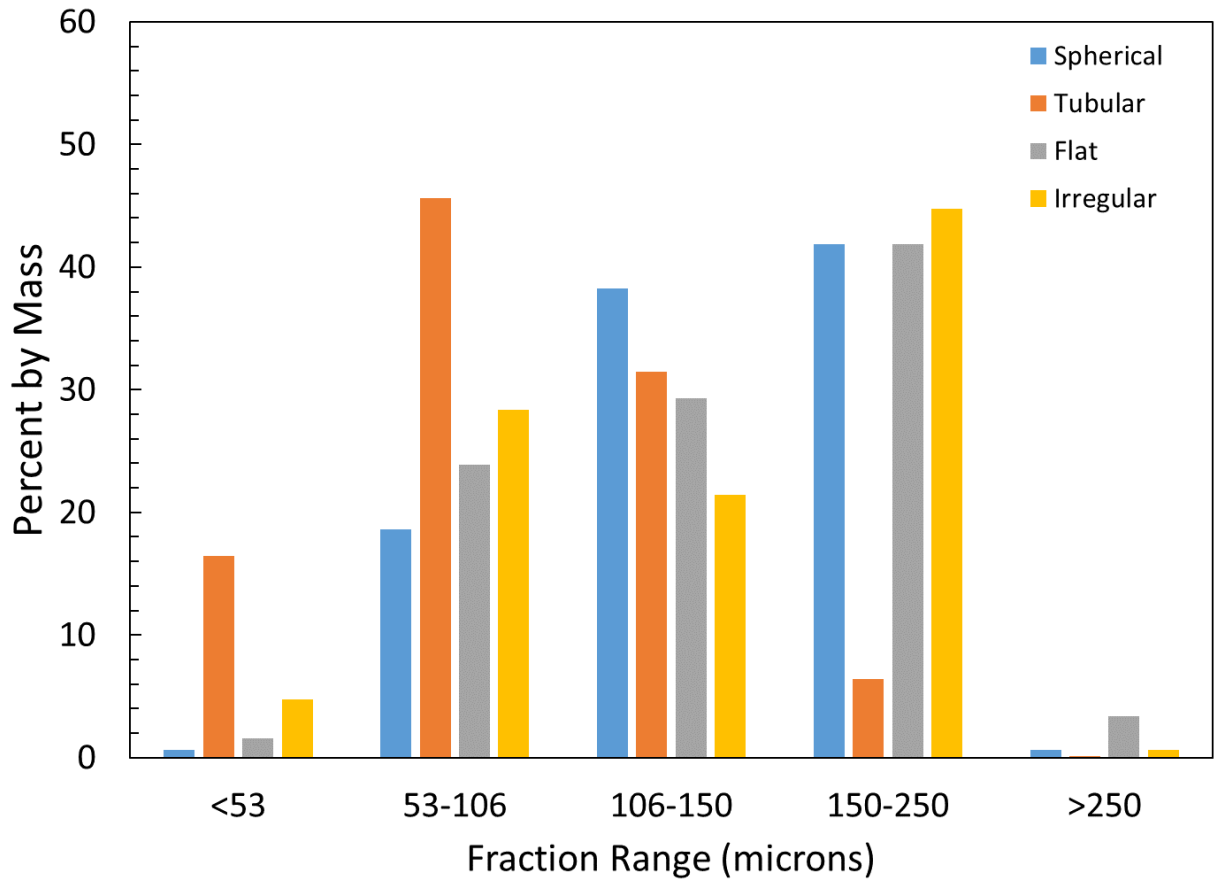


Fig. S1. Sieved powder size fractions by mass percent abundance.

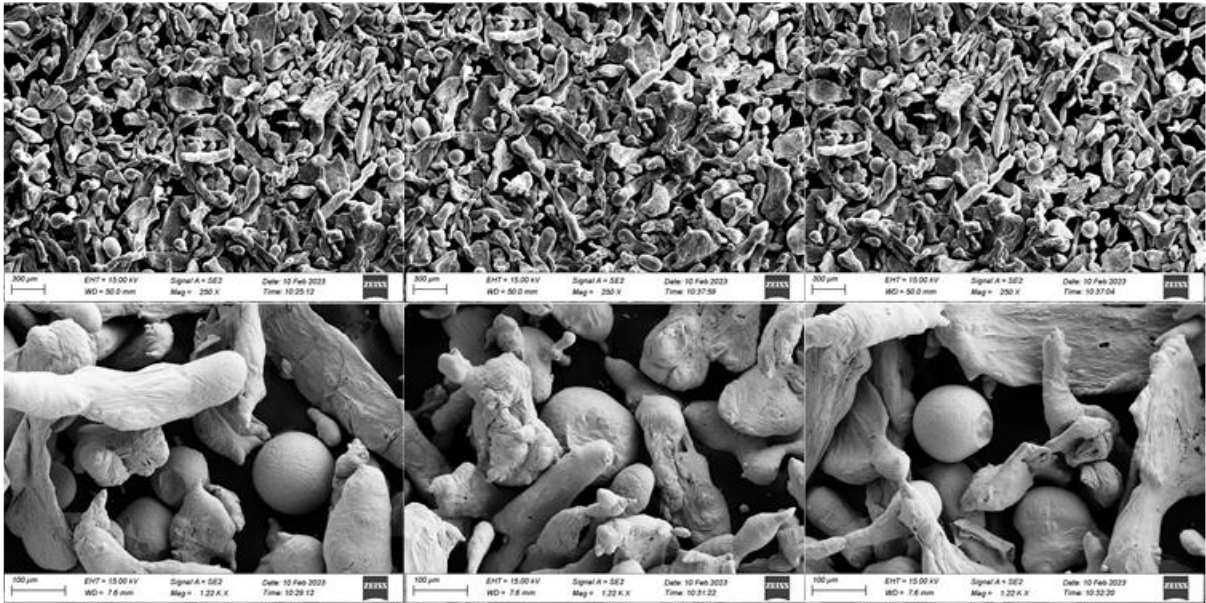


Fig. S2. Bulk Mixed SEM images.

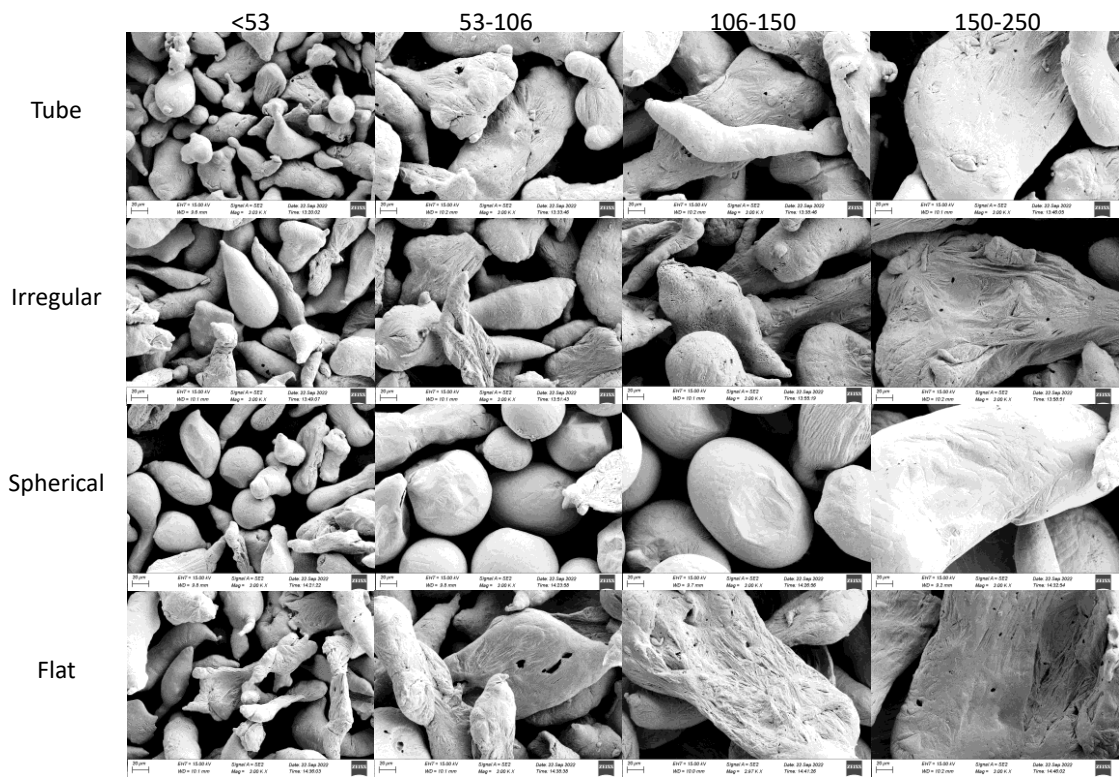
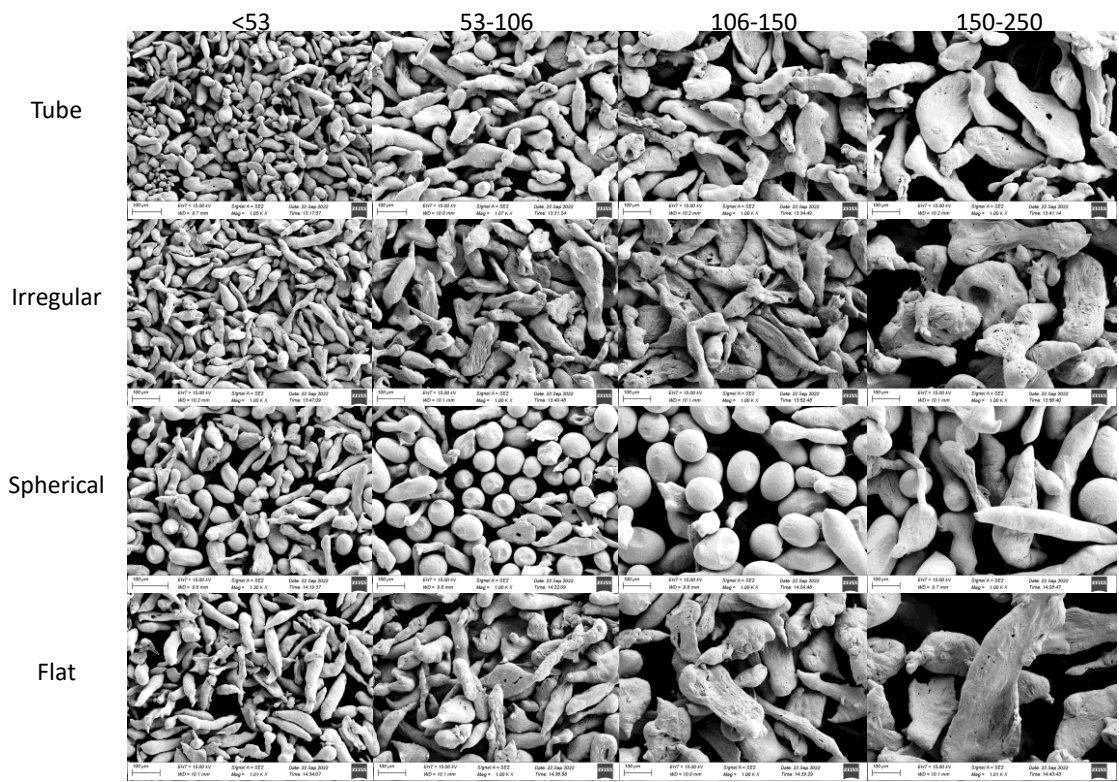


Fig. S3. 100 micron and 20 micron scaled images.

Shape	Sieve	BET cm ² /g	D10 micron	D50 micron	D90 micron	VMD micron	Aspect Ratio s50	Convexity s50	Elongation s50	Sphericity s50	straightness s50
Irregular	<53	600	47	63	81	63	0.552	0.849	0.316	0.75	0.992
Irregular	53-106	620	63	90	124	91	0.546	0.863	0.291	0.748	0.981
Irregular	106-150	550	84	122	165	124	0.526	0.856	0.252	0.726	0.962
Irregular	150-250	560	89	148	212	151	0.506	0.848	0.23	0.711	0.953
Spherical	<53	190	46	60	74	61	0.693	0.888	0.471	0.838	0.994
Spherical	53-106	220	73	98	126	98	0.875	0.942	0.708	0.927	0.994
Spherical	106-150	140	111	135	167	137	0.845	0.953	0.668	0.927	0.994
Spherical	150-250	130	138	176	210	176	0.702	0.955	0.496	0.892	0.993
Tubular	<53	690	34	52	69	52	0.615	0.854	0.382	0.784	0.993
Tubular	53-106	480	58	81	109	83	0.584	0.873	0.328	0.772	0.99
Tubular	106-150	440	63	101	143	103	0.558	0.865	0.289	0.751	0.976
Tubular	150-250	450	62	105	168	112	0.552	0.861	0.277	0.743	0.972
Flat/Planar	<53	540	37	55	72	55	0.581	0.847	0.338	0.758	0.992
Flat/Planar	53-106	320	73	99	131	101	0.543	0.876	0.295	0.755	0.983
Flat/Planar	106-150	300	103	137	174	139	0.513	0.859	0.245	0.722	0.96
Flat/Planar	150-250	290	137	184	250	188	0.476	0.829	0.198	0.678	0.941

Fig. S4. BET surface area data for untreated, sieved particle fractions by shape.

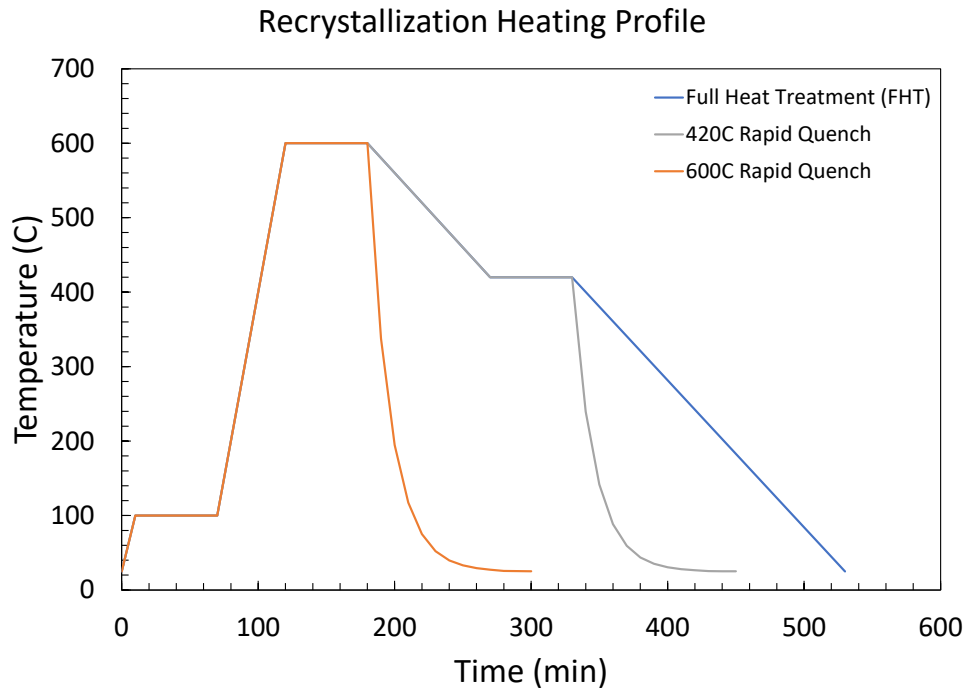


Fig. S5. Temperature profiles for the various recrystallization treatments.

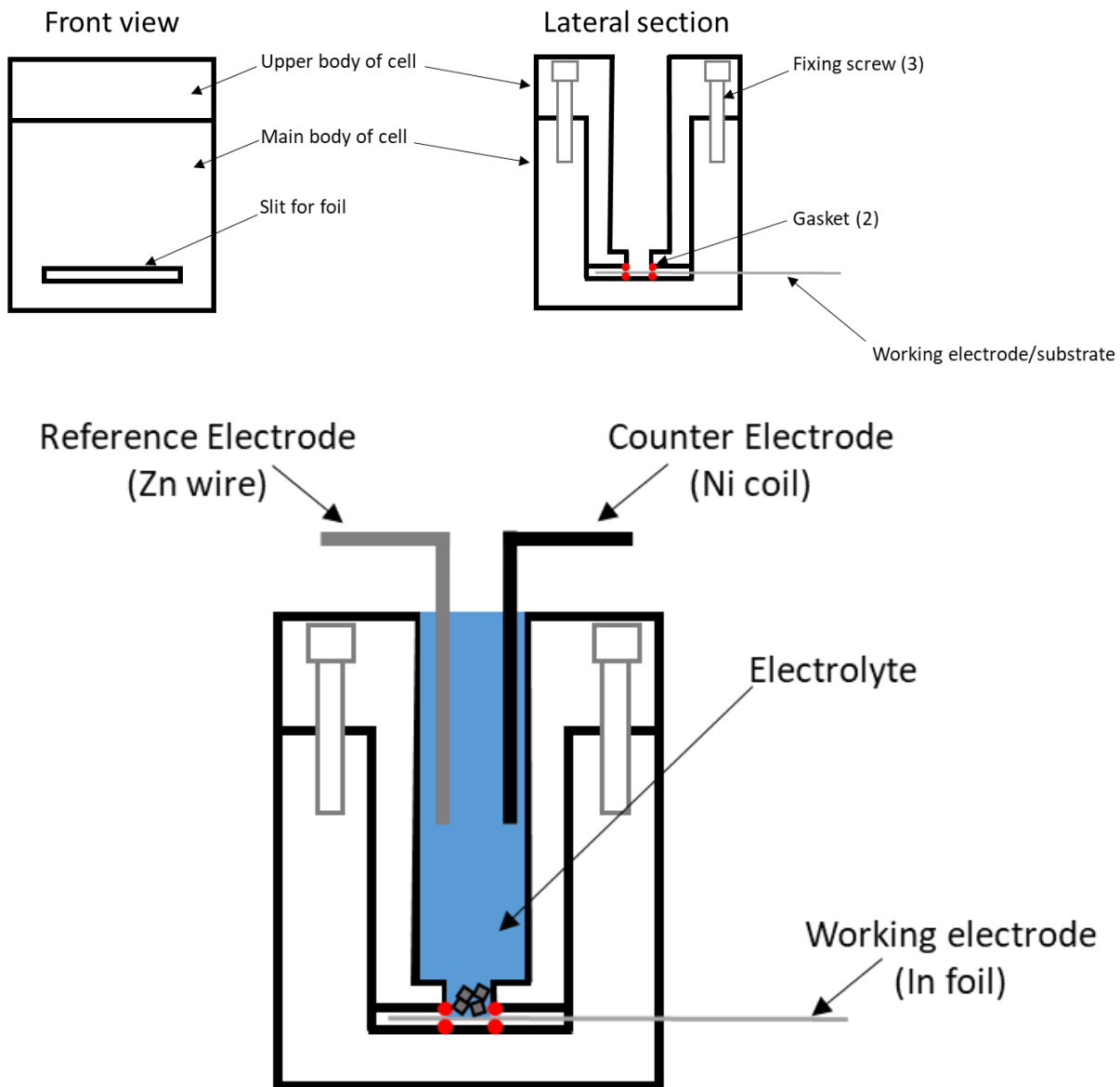


Fig. S6. Schematic of the custom-built 3-electrode cell.

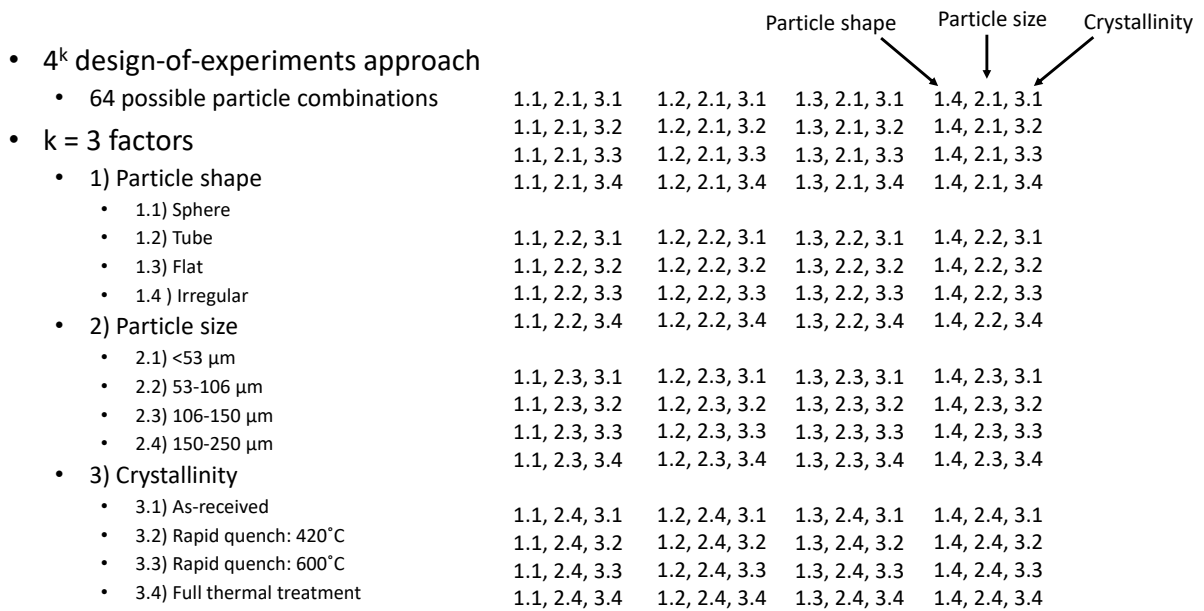


Fig. S7. DOE matrix organization and definitions for zinc powder.

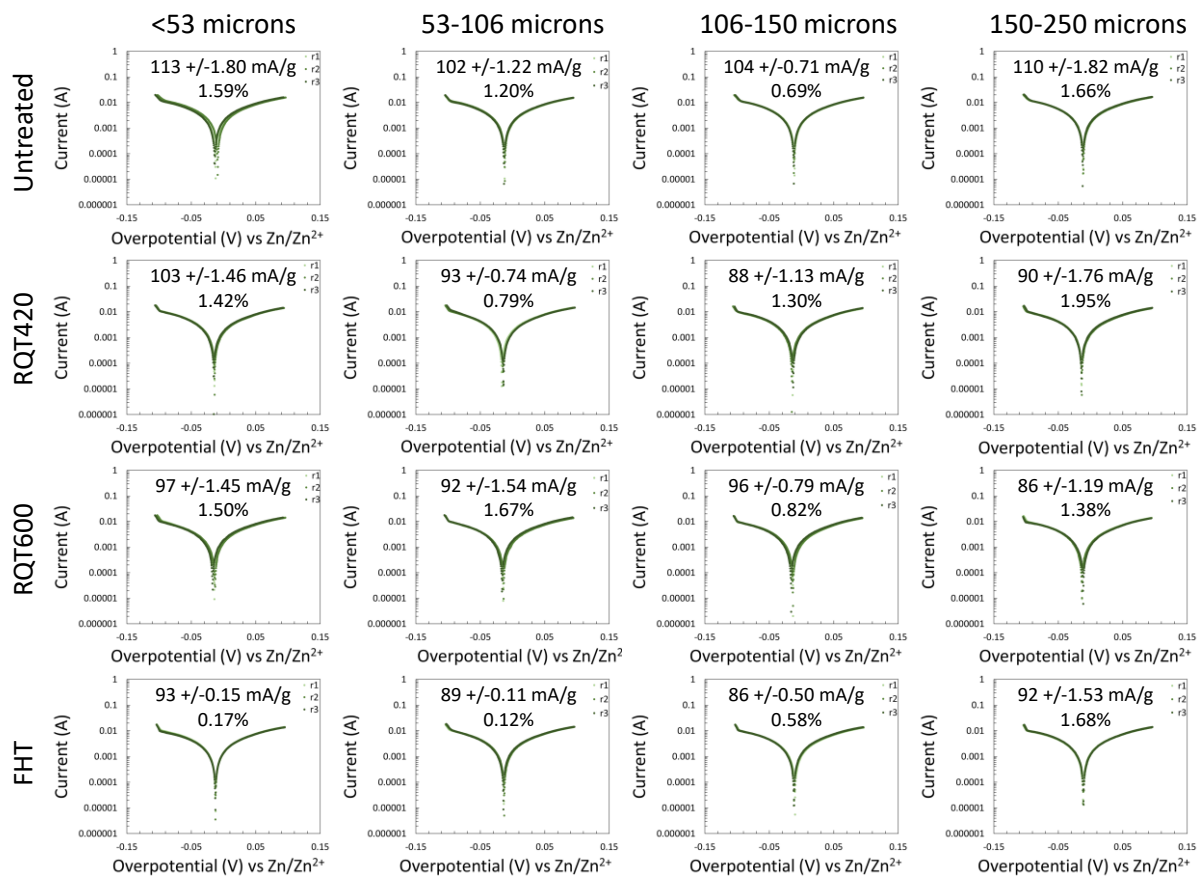


Fig. S8. Tube shaped powder LSVs.

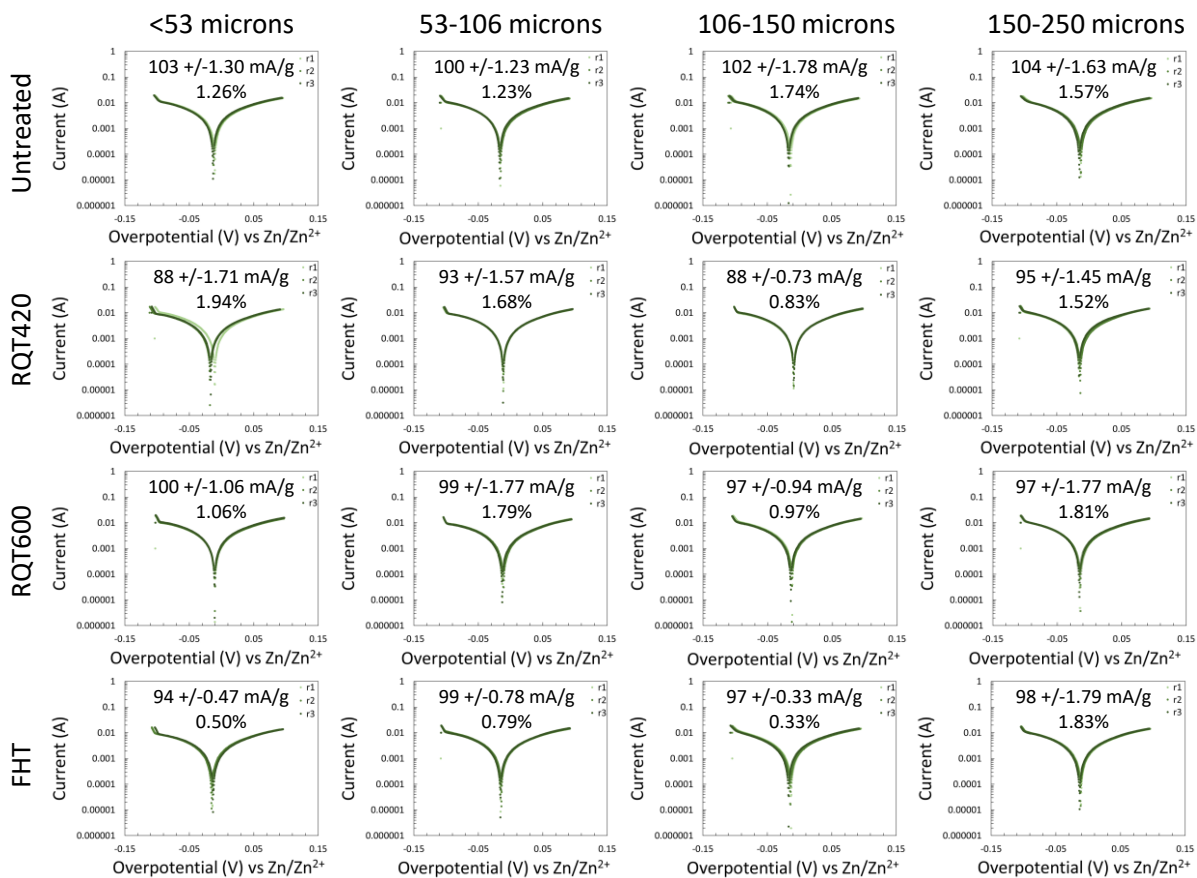


Fig. S9. Flat shaped powder LSVs

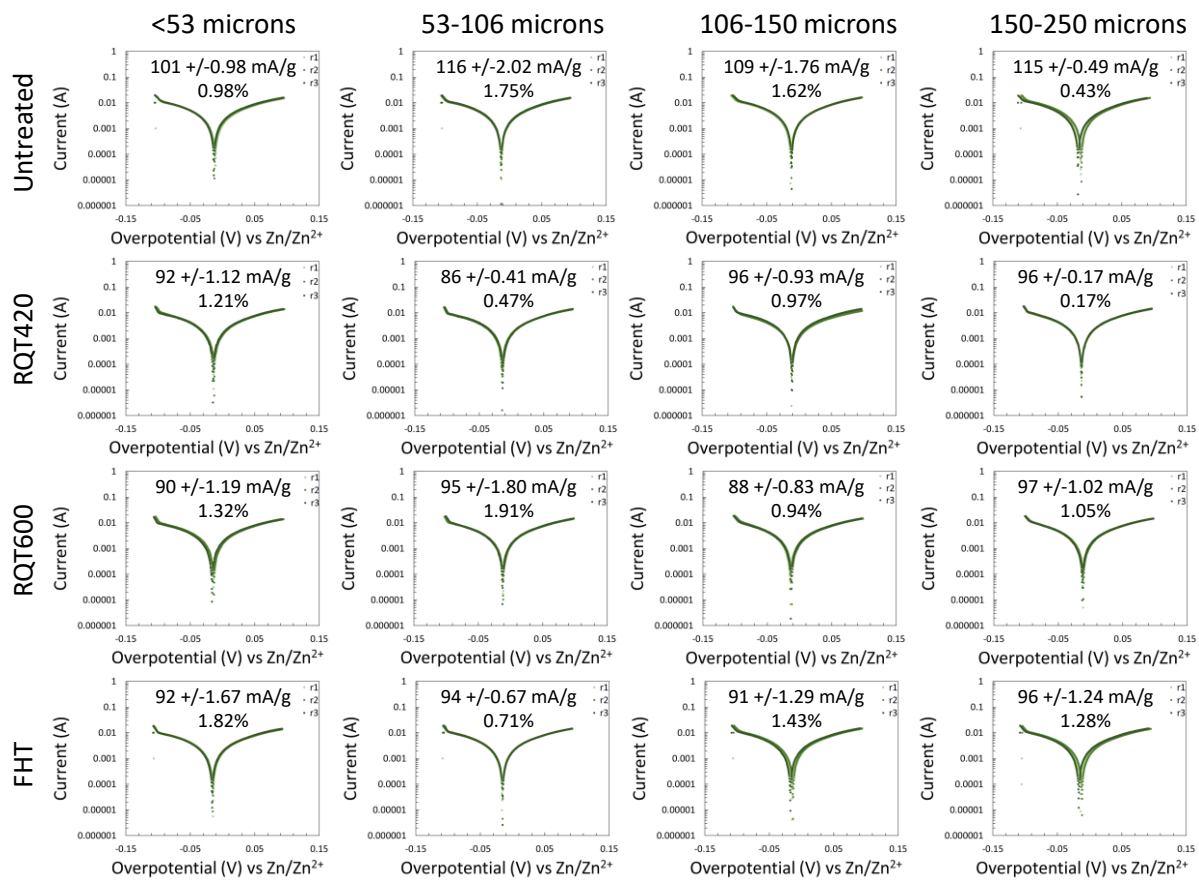


Fig. S10. Irregular shaped powder LSVs

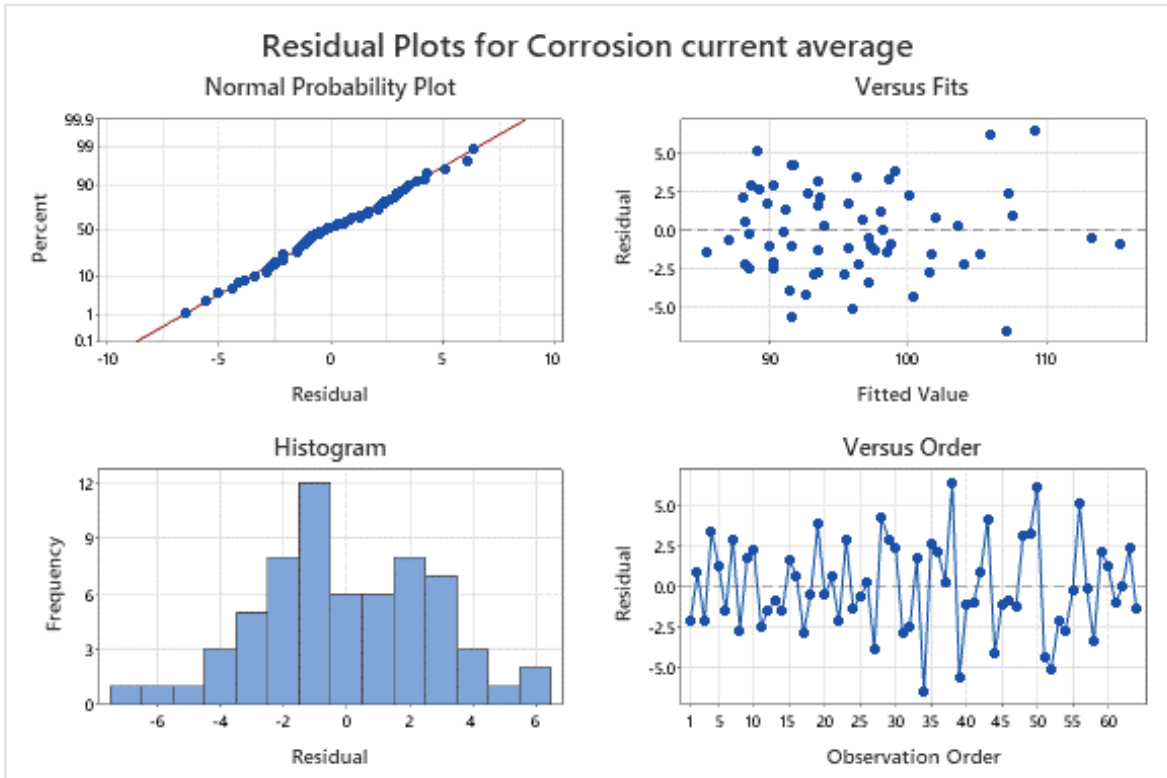


Fig. S11. LSV powder DOE residuals – corrosion current.

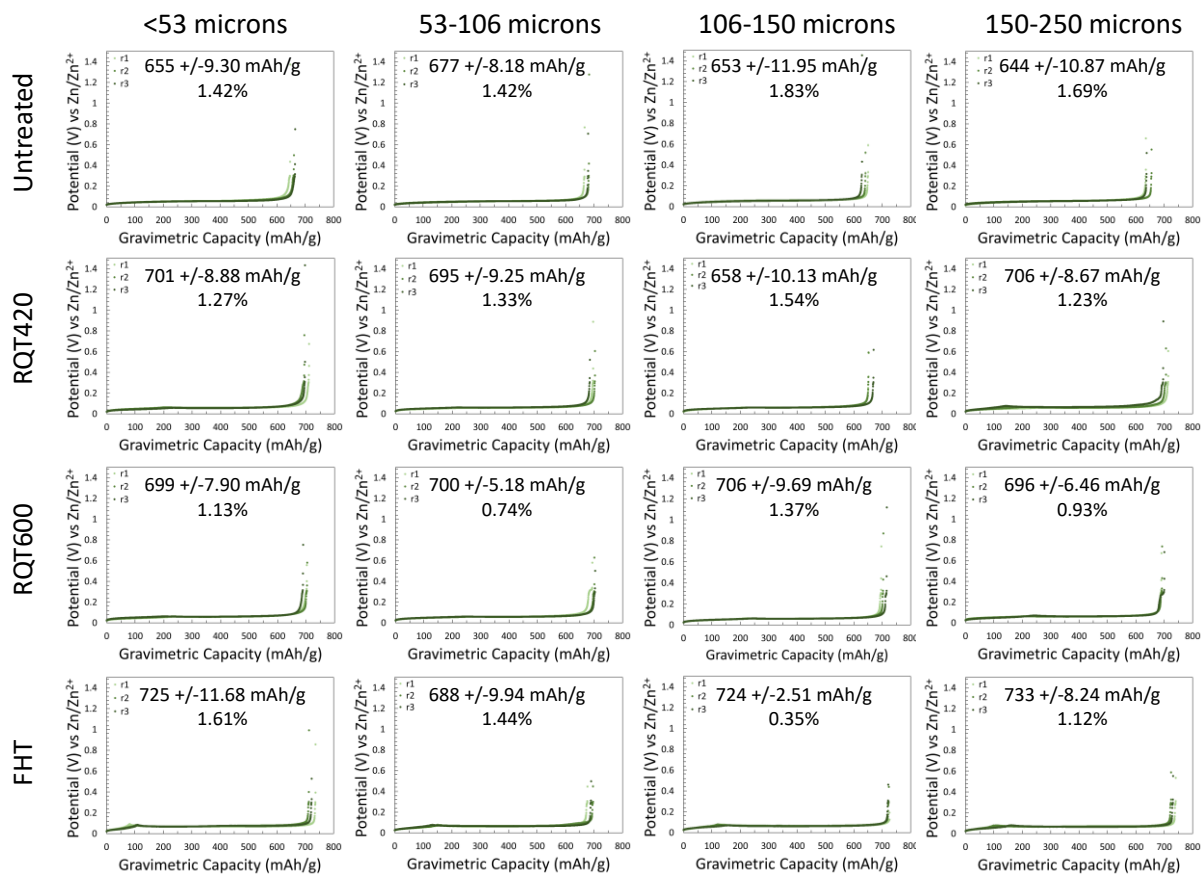


Fig. S12. Tube shaped powder CCDs.

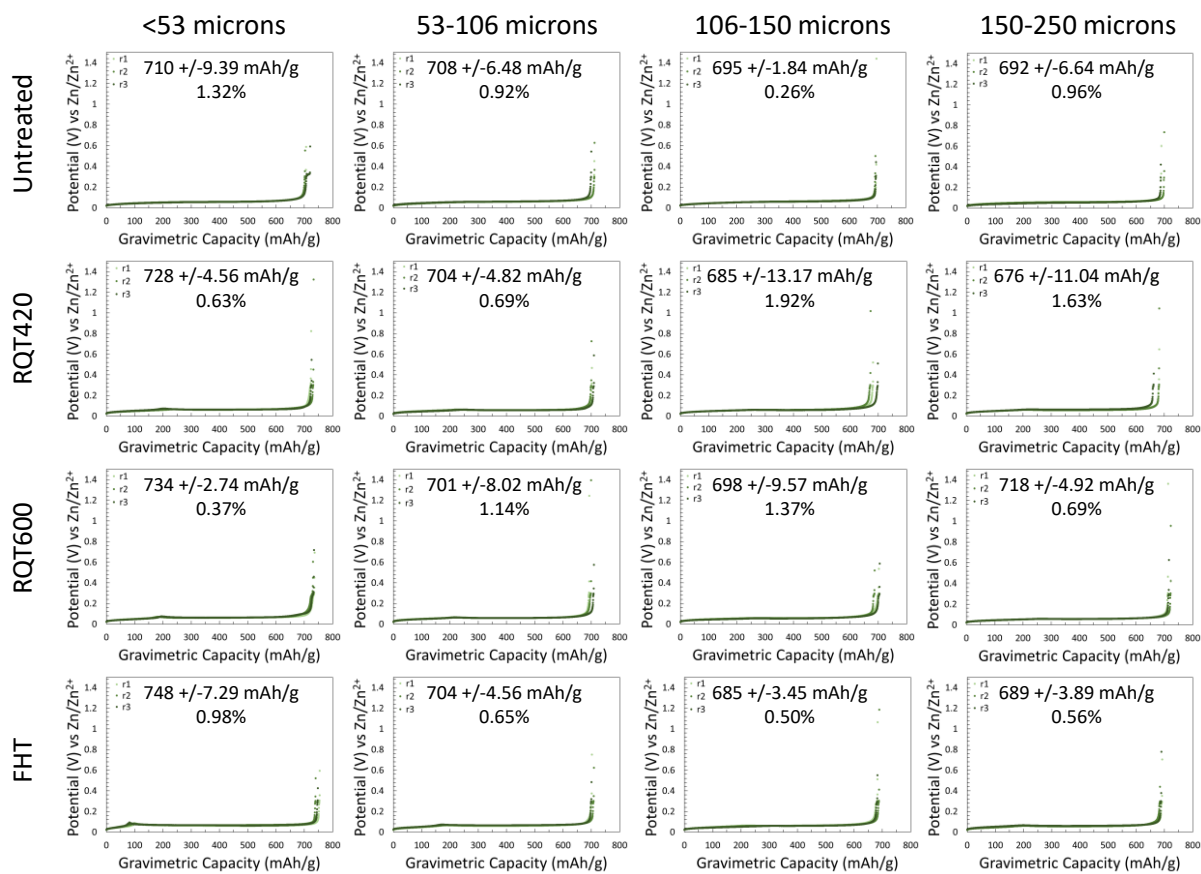


Fig. S13. Flat shaped powder CCDs.

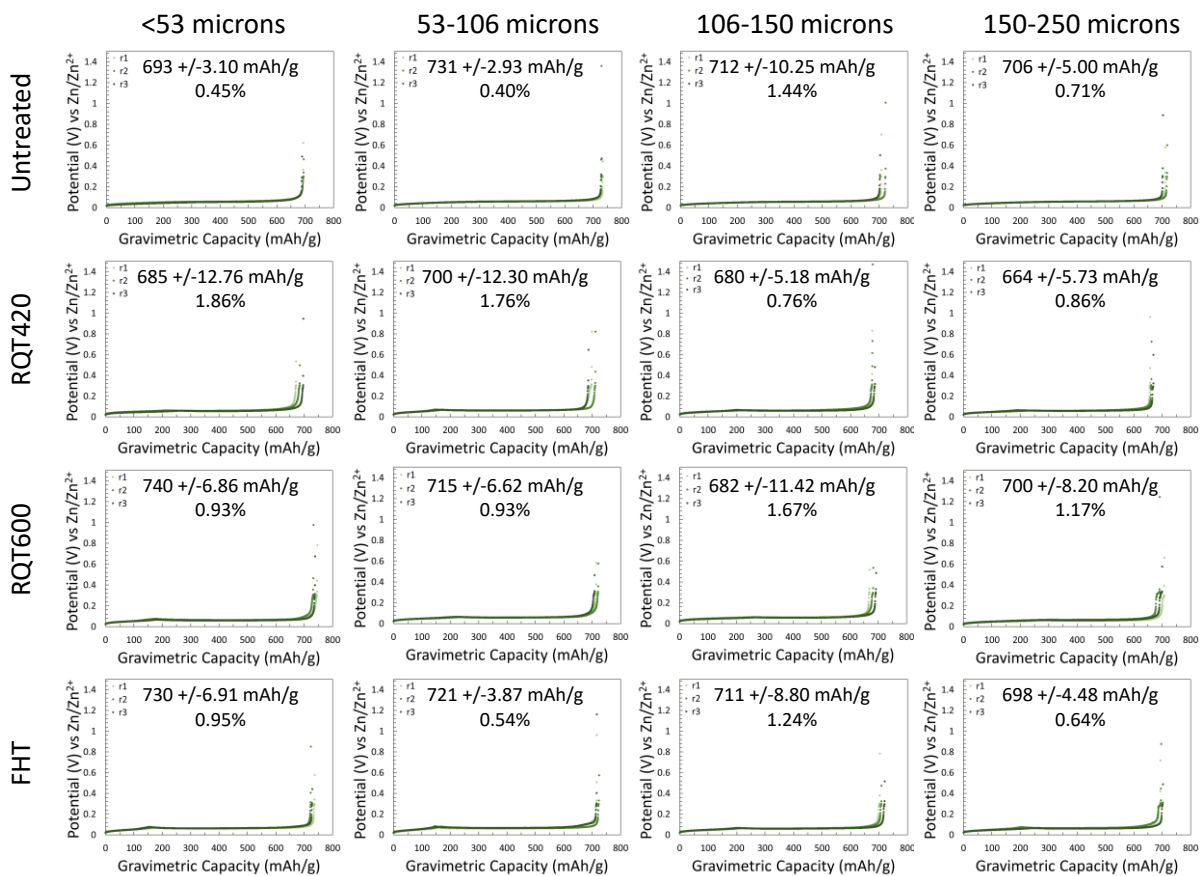


Fig. S14. Irregular shaped powder CCDs.

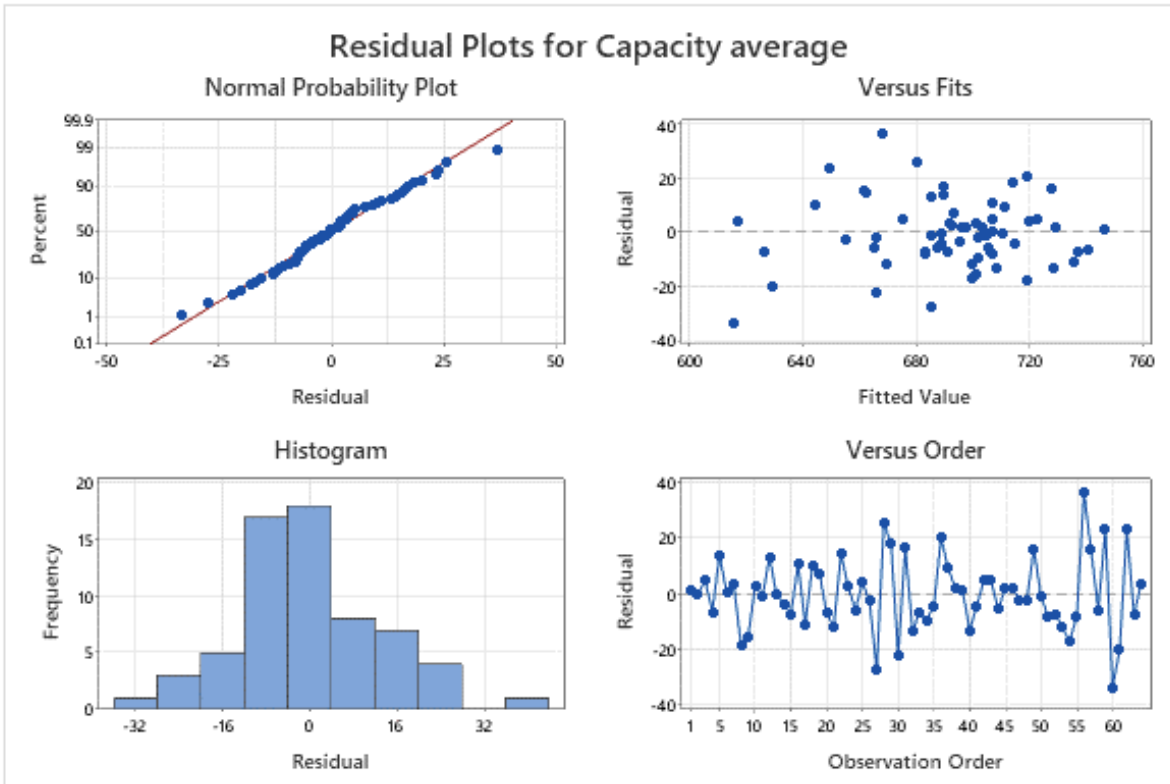


Fig. S15. CCD powder DOE residuals – achieved capacity.

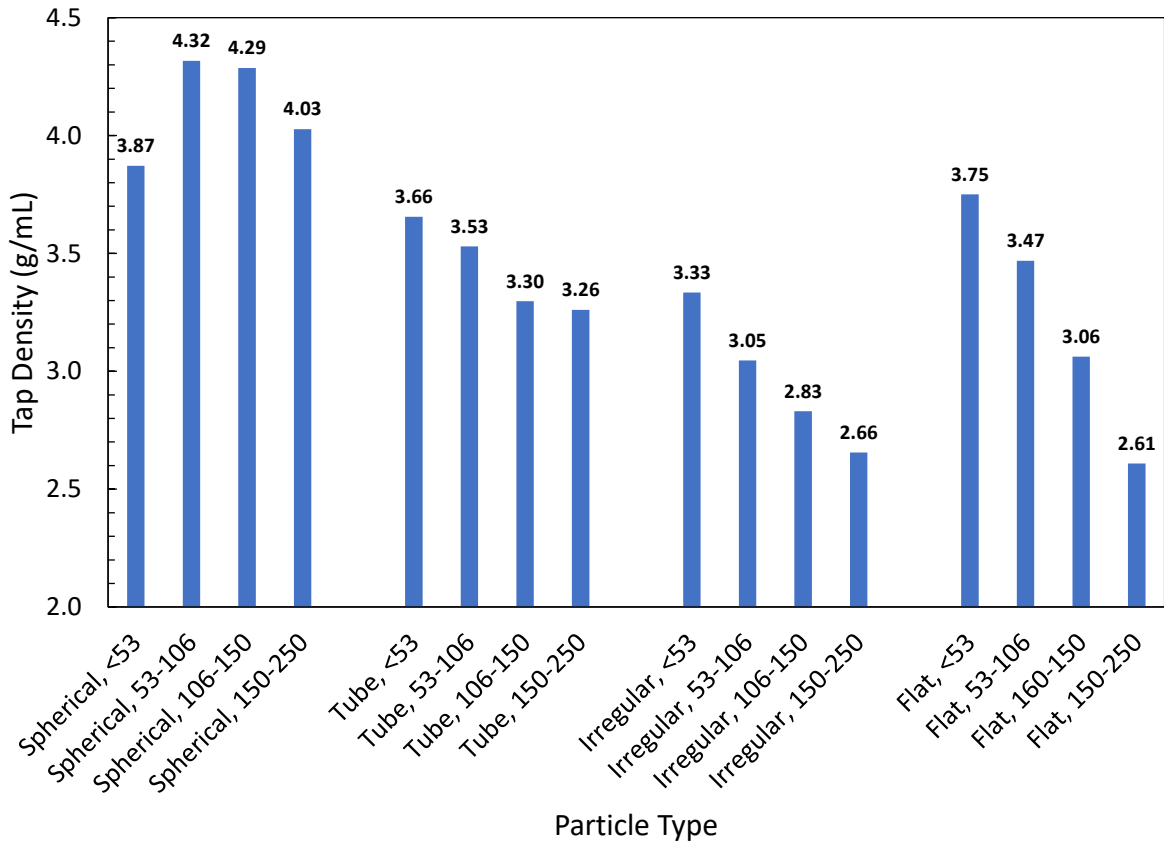


Fig. S16. Bulk powder tap densities.

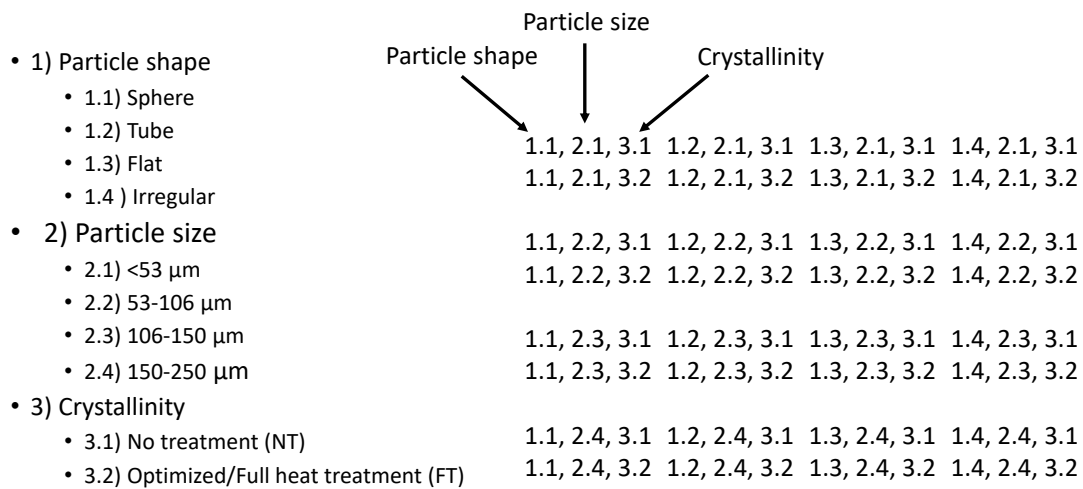


Fig. S17. DOE matrix organization and definitions for zinc slurry.

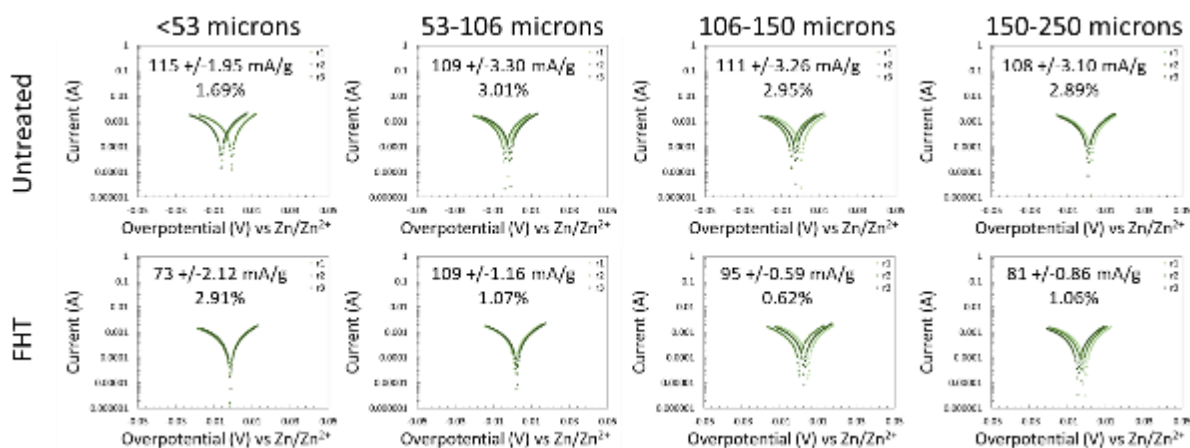


Fig. S18. Tube slurry LPR measurements.

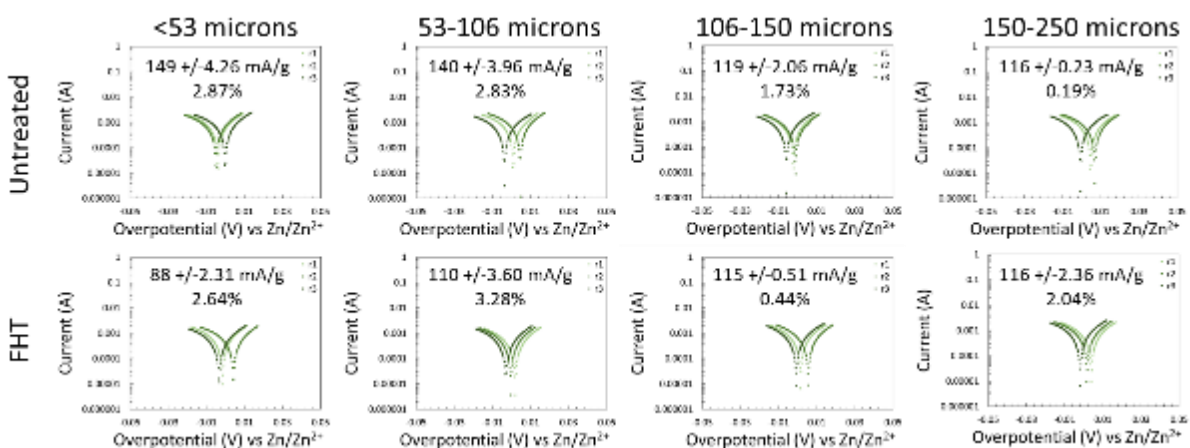


Fig. S19. Flat slurry LPR measurements.

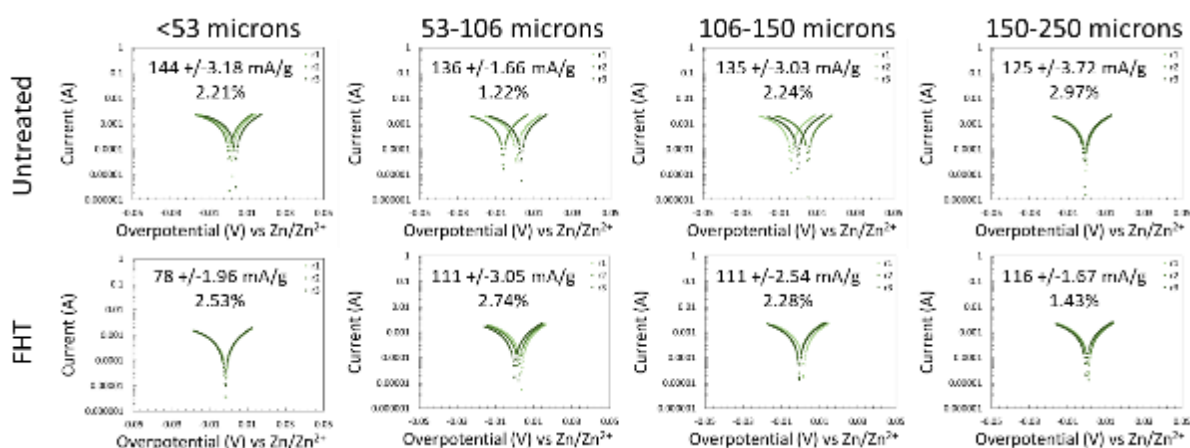


Fig. S20. Irregular shaped slurry LPR measurements.

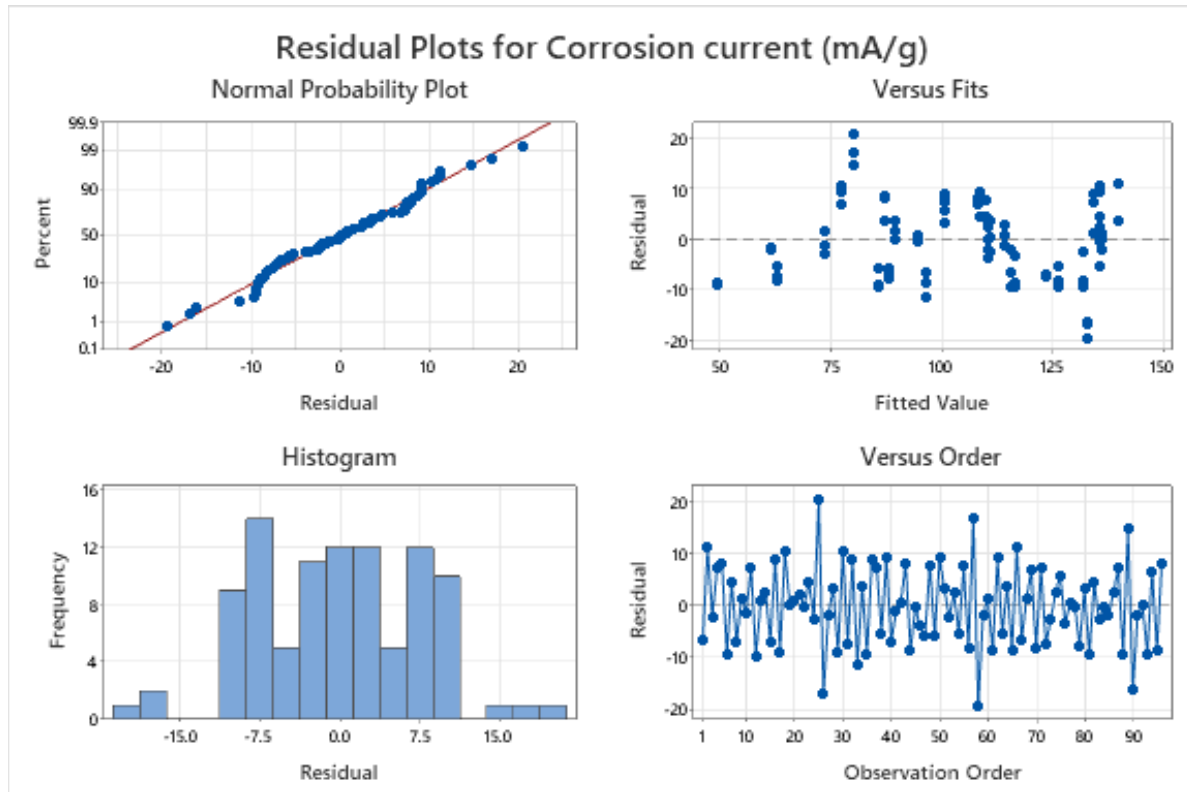


Fig. S21. Slurry LPR DOE residuals – corrosion current.

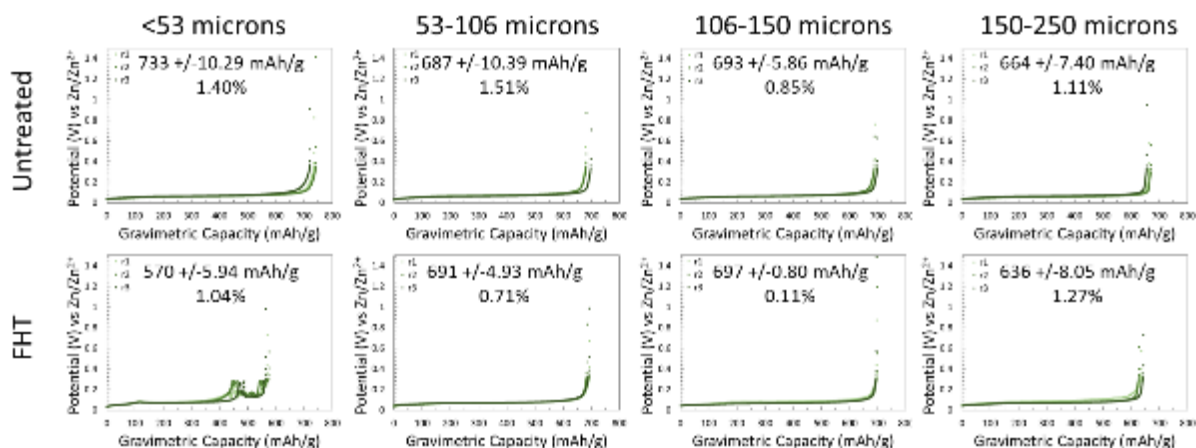


Fig. S22. Tube slurry CCDs.

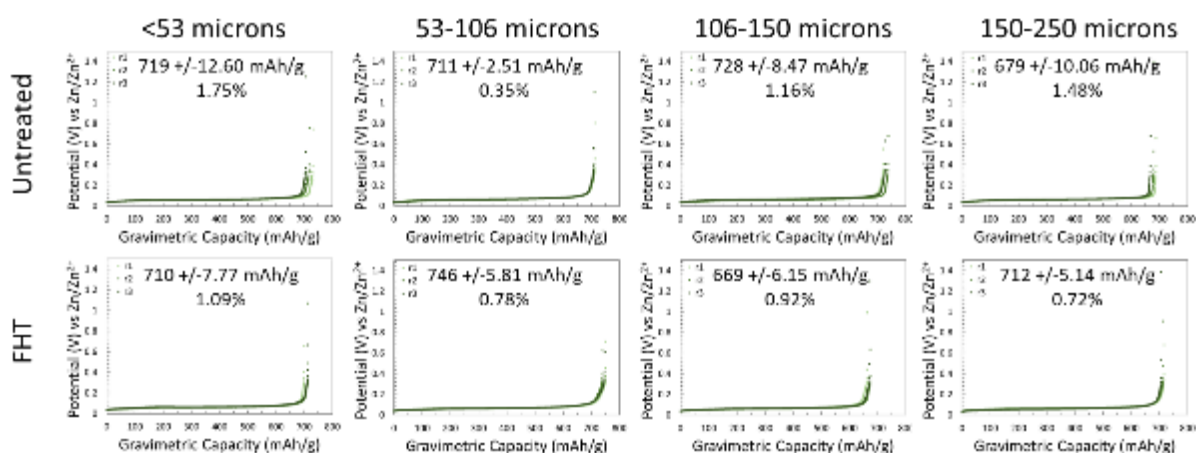


Fig. S23. Flat slurry CCDs.

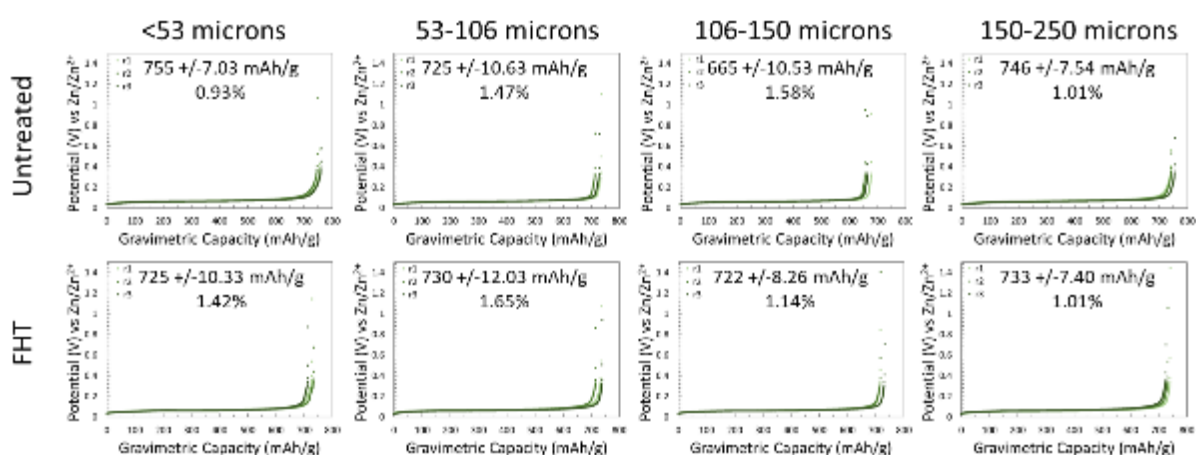


Fig. S24. Irregular slurry CCDs.

Residual Plots for Capacity (mAh/g)

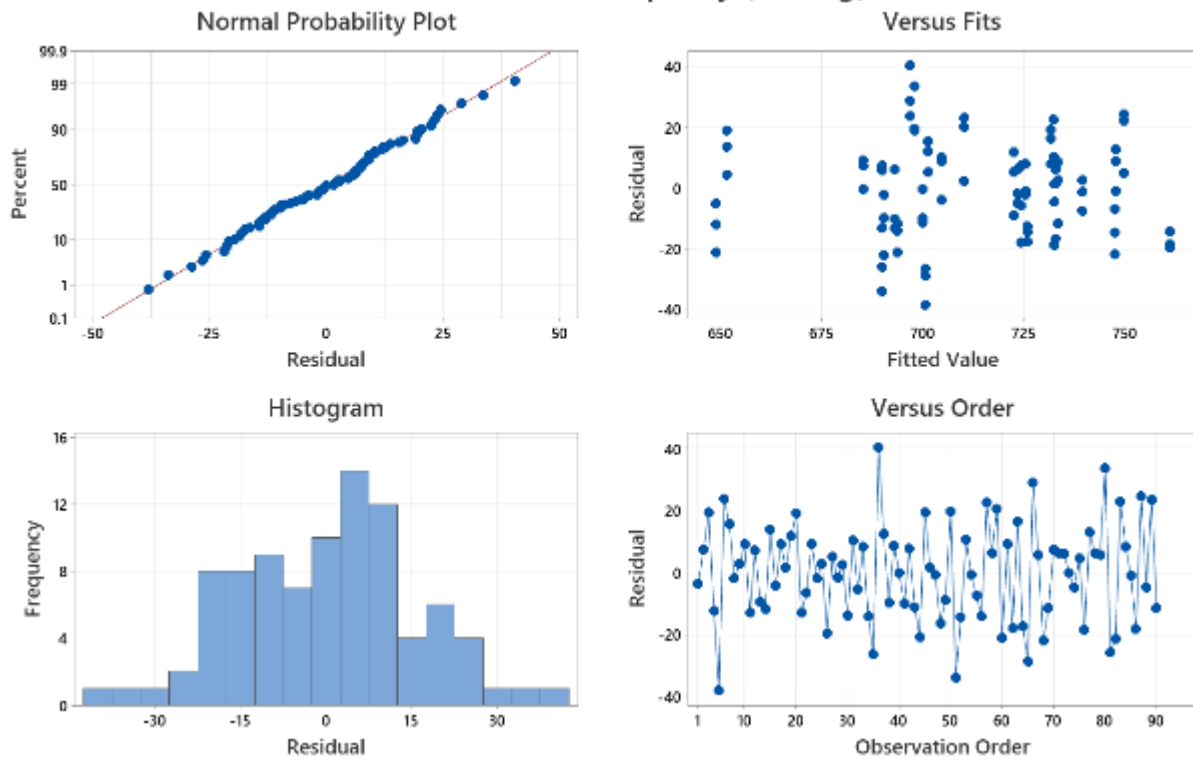


Fig. S25. Slurry CCD DOE residuals – achieved capacity

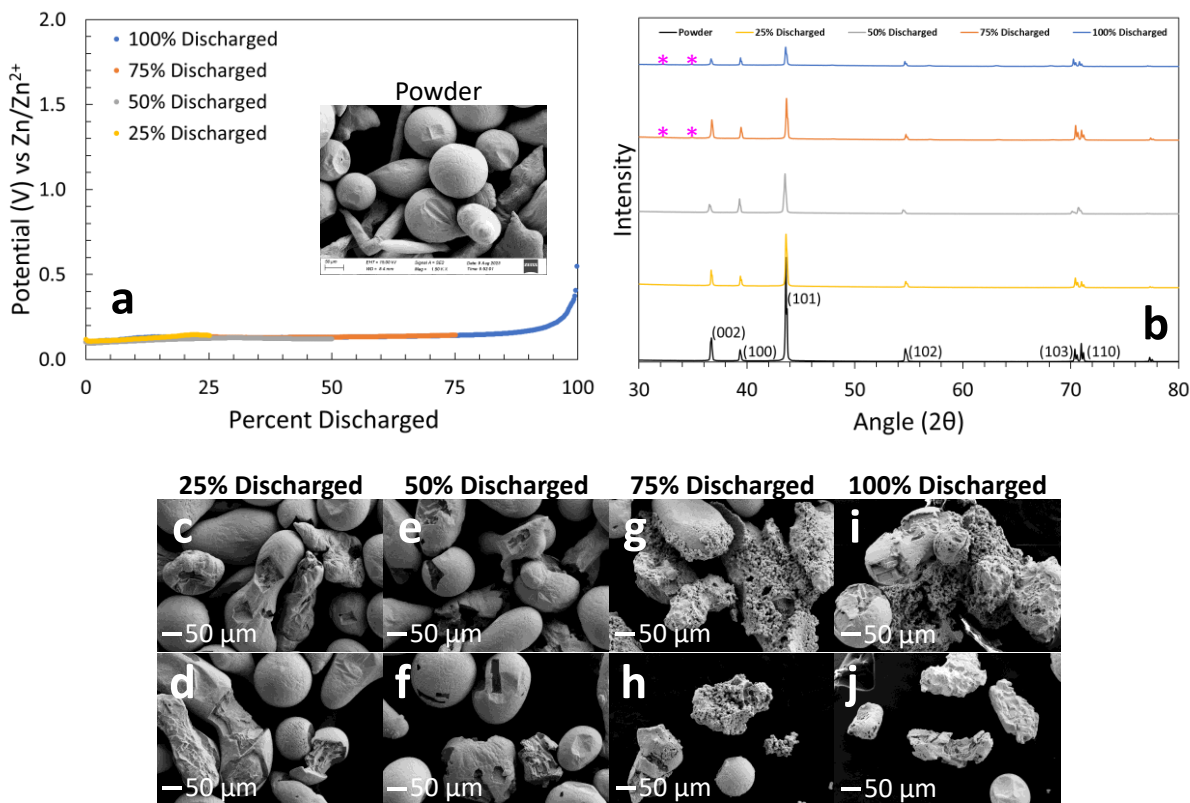


Fig. S26. a) Potential profile of zinc slurry oxidized to various percentages of discharge. A SEM image of rinsed powder is inset. b) Diffractograms of powders extracted from slurries oxidized to various percentages of discharge. c-j) Two sets of SEM images of zinc slurries oxidized to 25% (c, d), 50% (e, f), 75% (g, h), and 100% (i, j) discharge.

Fig. S26. Discussion

Slurry zinc anodes (unsieved, spherical, no heat treatment) were discharged at C/5 constant current discharge conditions in the 3-electrode cell to 25%, 50%, 75%, and 100% percent of discharge. The slurry discharge profiles are shown in panel a as well as a SEM image of undischarged powder inset. Once the discharge was ended, the zinc powder was promptly extracted, washed with 10% (v/v) acetic acid in water solution and then filtered and rinsed with copious amounts of water and ethanol before finally drying at 60C in an oven. Diffractograms of the discharged powders to various percentages (25%, 50%, 75%, and 100%) are shown in panel b and are compared to a fresh powder sample. Finally, a series of two sets of SEM images taken at 1500X magnification for the various percentage discharged powder samples can be seen in panels c-j.

The XRD shows some fluctuation in the dominating peak intensities (002, 100, and 101 lattices) as the discharge proceeds. There does seem to be some preferential dissolution at the 002 and 100 planes, judging by their relative intensities. To comment further on peak intensities, as the discharge proceeds and zinc continues to dissolve, less extractable zinc is present at 75% and 100% and this is reflected in their dwindling relative intensities. Turning to the SEM images, shape change in the dissolving zinc particles is observed at just 25% discharge. Continuing into deeper states of discharge, the particles continue to hollow out. Upon closer examination of the dissolution sites in the 25% and 50% particles,

there seems to be specific regions of the particle dissolving. Compared to the fresh powder sample image inset panel a, the spheres are no longer perfect. There appears to be slight nodules protruding and receding in the particle surface, likely where the manufactured zinc was freed from its substrate. These nodules appear to be preferential sites for dissolution in the early stages of discharge. At the 75% and 100% discharges it becomes difficult to discern shape as the change from the original particle is significant, and additionally, zinc oxide becomes present. The presence of zinc oxide is also reflected in the 75% and 100% discharge XRD patterns, indicated by the pink stars at 31° and 33° . EDS was performed on these samples as well, but no additional, useful information was gleaned.

Sphere				
	As-received	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	112.16	1.81	1.61
	53-106	90.83	1.45	1.60
	106-150	93.78	1.54	1.65
	150-250	98.15	1.66	1.69
	420C quench	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	96.09	1.40	1.46
	53-106	88.23	0.40	0.46
	106-150	95.88	0.43	0.44
	150-250	95.23	0.87	0.91
	600C quench	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	90.91	1.59	1.75
	53-106	94.24	1.36	1.44
	106-150	92.49	0.96	1.04
	150-250	84.03	0.87	1.03
	Full Treatment	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	101.94	1.06	1.04
	53-106	86.12	1.54	1.79
	106-150	90.97	1.48	1.62
	150-250	89.00	0.56	0.63

Table S1. Powder, spheres corrosion current.

Tube				
	As-received	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	112.81	1.80	1.59
	53-106	101.89	1.22	1.20
	106-150	103.93	0.71	0.69
	150-250	109.75	1.82	1.66
	420C quench	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	102.88	1.46	1.42
	53-106	93.10	0.74	0.79
	106-150	87.60	1.13	1.30
	150-250	90.35	1.76	1.95
	600C quench	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	96.68	1.45	1.50
	53-106	92.23	1.54	1.67
	106-150	95.89	0.79	0.82
	150-250	86.01	1.19	1.38
	Full Treatment	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	92.63	0.15	0.17
	53-106	88.86	0.11	0.12
	106-150	86.40	0.50	0.58
	150-250	91.58	1.53	1.68

Table S2. Powder, tubes corrosion current.

Flat				
	As-received	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	102.88	1.30	1.26
	53-106	100.12	1.23	1.23
	106-150	102.33	1.78	1.74
	150-250	103.70	1.63	1.57
	420C quench	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	88.07	1.71	1.94
	53-106	93.22	1.57	1.68
	106-150	87.87	0.73	0.83
	150-250	95.20	1.45	1.52
	600C quench	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	99.80	1.06	1.06
	53-106	98.89	1.77	1.79
	106-150	96.95	0.94	0.97
	150-250	97.49	1.77	1.81
	Full Treatment	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	94.27	0.47	0.50
	53-106	99.39	0.78	0.79
	106-150	97.43	0.33	0.33
	150-250	97.95	1.79	1.83

Table S3. Powder, flats corrosion current.

Irregular				
	As-received	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	100.65	0.98	0.98
	53-106	115.57	2.02	1.75
	106-150	108.58	1.76	1.62
	150-250	114.55	0.49	0.43
	420C quench	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	91.90	1.12	1.21
	53-106	86.01	0.41	0.47
	106-150	95.95	0.93	0.97
	150-250	96.34	0.17	0.17
	600C quench	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	90.19	1.19	1.32
	53-106	94.52	1.80	1.91
	106-150	88.44	0.83	0.94
	150-250	96.68	1.02	1.05
	Full Treatment	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	91.57	1.67	1.82
	53-106	94.18	0.67	0.71
	106-150	90.59	1.29	1.43
	150-250	96.20	1.24	1.28

Table S4. Powder, irregulars' corrosion current.

Sphere				
	As-received	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	703.56	10.44	1.48
	53-106	682.73	6.92	1.01
	106-150	659.80	6.54	0.99
	150-250	672.86	7.46	1.11
	420C quench	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	698.82	3.44	0.49
	53-106	675.29	6.72	0.99
	106-150	672.70	1.84	0.27
	150-250	619.25	6.45	1.04
	600C quench	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	684.09	7.52	1.10
	53-106	704.75	6.13	0.87
	106-150	582.20	6.71	1.15
	150-250	620.92	4.62	0.74
	Full Treatment	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	743.77	4.83	0.65
	53-106	657.67	8.99	1.37
	106-150	677.72	0.69	0.10
	150-250	609.53	9.14	1.50

Table S5. Powder, spheres achieved capacity.

Tube				
	As-received	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	654.49	9.30	1.42
	53-106	676.65	8.18	1.21
	106-150	652.81	11.95	1.83
	150-250	643.55	10.87	1.69
	420C quench	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	700.95	8.88	1.27
	53-106	695.18	9.25	1.33
	106-150	658.43	10.13	1.54
	150-250	706.42	8.67	1.23
	600C quench	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	699.28	7.90	1.13
	53-106	699.58	5.18	0.74
	106-150	706.11	9.69	1.37
	150-250	695.63	6.46	0.93
	Full Treatment	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	724.79	11.68	1.61
	53-106	688.19	9.94	1.44
	106-150	724.03	2.51	0.35
	150-250	732.53	8.24	1.12

Table S6. Powder, tubes achieved capacity.

Flat				
	As-received	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	710.06	9.39	1.32
	53-106	707.63	6.48	0.92
	106-150	694.87	1.84	0.26
	150-250	692.14	6.64	0.96
	420C quench	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	727.83	4.56	0.63
	53-106	704.29	4.82	0.69
	106-150	684.55	13.17	1.92
	150-250	676.04	11.04	1.63
	600C quench	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	734.05	2.74	0.37
	53-106	700.80	8.02	1.14
	106-150	698.37	9.57	1.37
	150-250	717.96	4.92	0.69
	Full Treatment	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	747.72	7.29	0.98
	53-106	704.14	4.56	0.65
	106-150	685.31	3.45	0.50
	150-250	688.80	3.89	0.56

Table S7. Powder, flats achieved capacity.

Irregular				
	As-received	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	692.75	3.10	0.45
	53-106	731.47	2.93	0.40
	106-150	711.88	10.25	1.44
	150-250	705.81	5.00	0.71
	420C quench	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	684.85	12.76	1.86
	53-106	699.58	12.30	1.76
	106-150	680.15	5.18	0.76
	150-250	663.59	5.73	0.86
	600C quench	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	739.52	6.86	0.93
	53-106	715.22	6.62	0.93
	106-150	681.97	11.42	1.67
	150-250	699.88	8.20	1.17
	Full Treatment	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	730.10	6.91	0.95
	53-106	720.54	3.87	0.54
	106-150	710.66	8.80	1.24
	150-250	697.91	4.48	0.64

Table S8. Powder, irregulars achieved capacity.

Sphere				
	Untreated	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	115.48	1.67	1.44
	53-106	91.28	1.71	1.87
	106-150	86.25	1.99	2.31
	150-250	94.03	2.83	3.01
	FHT	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	97.68	2.92	2.99
	53-106	59.89	0.14	0.23
	106-150	40.43	0.29	0.72
	150-250	55.76	1.58	2.83

Table S9. Slurry, spheres corrosion current.

Tube				
	Untreated	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	115.17	1.95	1.69
	53-106	109.41	3.30	3.01
	106-150	110.23	3.26	2.95
	150-250	107.51	3.10	2.89
	FHT	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	72.77	2.12	2.91
	53-106	109.07	1.17	1.07
	106-150	94.91	0.59	0.62
	150-250	81.45	0.86	1.06

Table S10. Slurry, tubes corrosion current.

Flat				
	Untreated	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	148.68	4.26	2.87
	53-106	140.06	3.96	2.83
	106-150	118.93	2.06	1.73
	150-250	116.48	0.23	0.19
	FHT	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	87.72	2.31	2.64
	53-106	109.72	3.60	3.28
	106-150	115.50	0.51	0.44
	150-250	115.67	2.36	2.04

Table S11. Slurry, flats corrosion current.

Irregular				
	Untreated	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	143.96	3.18	2.21
	53-106	135.94	1.66	1.22
	106-150	134.77	3.03	2.25
	150-250	125.13	3.73	2.98
	FHT	Corrosion Current Density (mA/g)	Standard Deviation (+/-) (mA/g)	Coefficient of Variation
	<53	77.57	1.96	2.53
	53-106	111.46	3.06	2.74
	106-150	111.38	2.54	2.28
	150-250	116.48	1.67	1.44

Table S12. Slurry, irregulars corrosion current.

Sphere				
	Untreated	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	737.54	5.16	0.70
	53-106	767.07	10.69	1.39
	106-150	633.02	8.07	1.27
	150-250	678.08	4.93	0.73
	FHT	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	727.22	5.47	0.75
	53-106	743.73	10.69	1.44
	106-150	723.20	5.61	0.78
	150-250	725.56	11.23	1.55

Table S13. Slurry, spheres achieved capacity.

Tube				
	Untreated	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	733.45	10.29	1.40
	53-106	687.41	10.39	1.51
	106-150	692.80	5.86	0.85
	150-250	663.87	7.40	1.11
	FHT	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	569.61	5.94	1.04
	53-106	690.63	4.93	0.71
	106-150	696.77	0.80	0.11
	150-250	636.15	8.05	1.27

Table S14. Slurry, tubes achieved capacity.

Flat				
	Untreated	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	718.96	12.60	1.75
	53-106	711.13	2.51	0.35
	106-150	727.82	8.47	1.16
	150-250	679.12	10.06	1.48
	FHT	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	709.83	7.77	1.09
	53-106	746.32	5.81	0.78
	106-150	669.37	6.15	0.92
	150-250	712.43	5.14	0.72

Table S15. Slurry, flats achieved capacity.

Irregular				
	Untreated	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	754.79	7.03	0.93
	53-106	725.33	10.63	1.47
	106-150	665.71	10.53	1.58
	150-250	746.24	7.54	1.01
	FHT	Average Achievable Capacity (mAh/g)	Standard Deviation (+/-) (mAh/g)	Coefficient of Variation
	<53	725.23	10.33	1.42
	53-106	729.83	12.03	1.65
	106-150	722.05	8.26	1.14
	150-250	733.34	7.40	1.01

Table S16. Slurry, irregulars achieved capacity.