

Supplementary Information

High-Rate Laminar Zn Plating in Aqueous Zinc Batteries: From S-PANI Grafted Bacterial Cellulose to Stable Metal Anode

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Experimental section

Chemicals:

Commercially available zinc and copper foils, as well as carbon sheets, were purchased from Merck and Redox Kala, respectively. All reagents, including zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 99.0%), hydrochloric acid (HCl , 37.0% w/w), aniline ($\text{C}_6\text{H}_5\text{NH}_2$, 99.5%), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, 98.0%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.8%), 1,2-dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$, 99.0%), cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 99.0%), copper sulfate hexahydrate ($\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$, 99.0%), trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99.0%), potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$, 99.0%), and chlorosulfonic acid (HSO_3Cl , 99.0 %) were also obtained from Merck and used without further purification. Deionized (DI) water was used throughout the experiment, which was supplied from the Zolalan water purification system.

Material Characterization

Field emission scanning electron microscopy (FE-SEM) images were acquired using a TESCAN (MIRA 3 LMU) microscope. Thermal gravimetric analysis (TGA) curves were measured on an SDT Q600 V20.9 instrument in the range of 25-800 °C. X-ray diffraction (XRD) patterns were obtained with a Philips PW1730 diffractometer. Fourier-transform infrared (FTIR) spectra were measured on a Perkin-Elmer instrument in the range of 500-4000 cm^{-1} . Atomic force microscopy (AFM) images were obtained using a VEECO CP-II microscope operated in non-contact-mode. Water contact angle (WCA) measurements were conducted using a CAG-20 contact angle meter.

Electrochemical Measurements

Electrochemical performance of zinc-based cells, encompassing Zn||Zn symmetrical cells, Zn||Cu half cells, and Zn||PBA full cells, was evaluated using a pouch-type cell. Long-term cycling and rate capability tests were conducted on an Atom Lab (Ataei Company, Isfahan, Iran). The Zn||Zn symmetrical cells were assembled with either untreated Zn foil or BC/S-PANI@BC@Zn composite electrodes as both anode and cathode, paired with a 1 M ZnSO_4 aqueous electrolyte and a Whatman filtration paper separator. For Zn||Cu half cells, the cathode was substituted with Cu foil, while retaining the 1 M ZnSO_4 electrolyte and filtration paper separator. Zn||PBA full cells were constructed with a synthesized PBA cathode, a filtration paper separator, an electrolyte of 1

M ZnSO₄, and either bare Zn or BC/S-PANI@BC@Zn as the anode. Electrochemical characterizations, including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and linear scanning voltammetry (LSV), were performed using an AutoLab 204 instrument. EIS measurements spanned a frequency range of 10⁺⁶ to 10⁻² Hz with an AC perturbation amplitude of 5 mV to assess impedance properties. Tafel polarization experiments were conducted in a three-electrode configuration, utilizing untreated Zn or BC/S-PANI@BC@Zn as the working electrode, a platinum foil counter electrode, and an Ag/AgCl reference electrode to investigate the electrochemical kinetics and corrosion characteristics.

Table S1. The xyz coordinates of the optimized structure for DFT calculation.

Atom	X	Y	Z
BC			
O	-1.52619300	0.96141100	-0.39304200
C	-3.58750100	-0.02892900	0.50783600
C	-1.69021800	-1.43266700	-0.40632100
C	-3.20333600	-1.33877700	-0.18821900
C	-1.19484500	-0.19171400	-1.16233600
C	-2.94329300	1.15958800	-0.23297500
H	-3.22166400	-0.05735100	1.54736100
H	-1.20058400	-1.47008600	0.57703900
H	-3.69962000	-1.35562100	-1.17188400
H	-1.67141600	-0.14084700	-2.15096200
H	-3.40739000	1.24968900	-1.22714700
O	0.17987700	-0.17696300	-1.45171600
C	1.13457200	-0.19077300	-0.38403400
O	3.12373900	0.98716800	0.41132300
C	3.98416800	-0.13414500	0.23785300
C	2.05801900	1.03699400	-0.55295200
C	1.98475000	-1.46237300	-0.48548400
H	4.40809800	-0.11293200	-0.78353000
H	0.63976500	-0.14265900	0.59188800
C	-3.11299200	2.47982600	0.50838000
H	-2.61375200	2.40921500	1.48749300
H	-4.17675000	2.65965500	0.67173200
O	-2.62160200	3.58488100	-0.23617500
H	-1.68899100	3.42135400	-0.43207800
O	-4.98732800	0.20718800	0.48763200
C	-5.73680800	-0.39739000	1.54132000
H	-5.71080700	-1.48907700	1.47984100
H	-6.76260000	-0.04034000	1.42640700
H	-5.35492400	-0.08138300	2.52319900
O	-3.64881100	-2.44381400	0.59133500

H	-3.26105300	-3.23569500	0.18798000
O	-1.45191000	-2.63382800	-1.12103500
H	-0.50767000	-2.84502500	-1.00255100
H	2.35829000	-1.53806100	-1.51757100
O	1.18723900	-2.61321100	-0.19140500
H	1.79209000	-3.36771100	-0.12071400
H	2.48383800	1.02011900	-1.56860700
C	1.36246900	2.37683200	-0.34209600
H	0.92977000	2.40794900	0.66827900
H	0.55707000	2.48030200	-1.06949800
O	2.25390900	3.46255700	-0.55266000
H	2.99271800	3.35415900	0.06199600
O	4.99701000	-0.10310600	1.18832400
C	5.98851900	0.90709200	0.98426400
H	5.56400700	1.90697400	1.11693900
H	6.42797700	0.82299100	-0.01860900
H	6.76070700	0.73617600	1.73560700
H	2.81412500	-1.38852700	1.50590400
C	3.17558300	-1.40942200	0.46794100
O	3.93816900	-2.58837000	0.22694400
H	4.68144400	-2.59942300	0.84622400

BC-Zn

O	1.47766700	-0.06966100	-0.91204800
C	3.76815400	0.00458000	0.11445700
C	1.93108700	1.60830500	0.89206200
C	2.89592500	0.47347600	1.29755000
C	0.93918500	1.09024800	-0.17314100
C	2.90259100	-0.27225300	-1.16025800
H	4.29860700	-0.90860400	0.41800600
H	1.32409200	1.90597600	1.75412200
H	3.55517000	0.79759900	2.10474400
H	0.64480100	1.87177900	-0.87063200

H	3.22265400	0.40279400	-1.96090700
O	-0.16739400	0.50574000	0.49441600
C	-1.46228500	0.39182200	-0.18312700
O	-3.70311400	1.15849600	-0.50121900
C	-4.34381300	0.00383000	0.07877700
C	-2.46870400	1.54743200	0.08917800
C	-2.06662700	-0.86936300	0.41622100
H	-4.49075200	0.18279700	1.15982200
H	-1.29631600	0.28473300	-1.26136000
C	2.95474300	-1.71045100	-1.67161900
H	3.98893200	-2.04801200	-1.77446100
H	2.42826100	-1.80630400	-2.62451300
O	2.27886800	-2.55004000	-0.67367100
H	2.40503600	-3.49227800	-0.86219000
O	4.68361900	1.05581300	-0.11143100
C	5.94343700	0.69771900	-0.71672900
H	5.80417000	0.34284200	-1.74465000
H	6.44908200	-0.06520400	-0.11472700
H	6.54051700	1.60882500	-0.73025700
O	2.13364500	-0.69954000	1.77070500
H	2.03558600	-0.67707300	2.73476600
O	2.60691500	2.74704600	0.43051400
H	3.50386800	2.52981800	0.11979700
H	-2.16266400	-0.75015200	1.50216500
O	-1.15237800	-2.01064600	0.20966100
H	-1.67572800	-2.82635700	0.34507100
H	-2.56297000	1.67942900	1.17847400
C	-2.12085300	2.89205100	-0.55011200
H	-2.09673300	2.78493300	-1.64319700
H	-2.91873200	3.59629900	-0.29339000
O	-0.85812700	3.31356200	-0.03849900
H	-0.75757900	4.26848600	-0.14945900
O	-5.52091400	-0.25273400	-0.56766800
C	-6.61744000	0.63977700	-0.26950400

H	-6.80800600	0.65935800	0.80971700
H	-7.48269200	0.23105000	-0.78960600
H	-6.40152100	1.64514400	-0.63880900
H	-3.35445000	-1.33138300	-1.26461100
C	-3.42189100	-1.20087400	-0.17542200
O	-3.80700100	-2.40289800	0.46474900
H	-4.67036900	-2.69382100	0.13236900
Zn	0.79007900	-1.54438700	0.40032100
S-PANI			
C	-5.61658200	-1.47373200	0.03990600
C	-7.17036200	0.52541800	1.19340100
C	-5.23390700	-0.13215400	-0.11554300
C	-6.76095200	-1.81777900	0.76194400
C	-7.53872200	-0.81348500	1.34020000
C	-6.02501400	0.86202800	0.46853200
H	-7.03691700	-2.86295700	0.84921300
H	-8.43171200	-1.07822900	1.89721900
H	-5.73609400	1.90269300	0.34998800
H	-7.77452100	1.31037700	1.63760100
N	-4.08851000	0.22412600	-0.92595800
H	-4.36981900	0.87618100	-1.65359500
H	-3.90629100	-1.46809900	-2.09066200
C	-2.89596700	0.67813200	-0.29198800
C	-0.47385600	1.55992900	0.86491100
C	-2.45894300	0.14773400	0.92968100
C	-2.11837900	1.65036000	-0.93268600
C	-0.92499000	2.07921000	-0.35701600
C	-1.26390700	0.59044900	1.49141300
H	-3.03280600	-0.62515300	1.42590100
H	-2.43887600	2.09698100	-1.86952000
H	-0.92788100	0.16561500	2.43311300
N	0.73143500	2.06255100	1.48854300
H	0.91095600	3.70866900	0.58351000

H	0.52185500	2.37555000	2.43343500
C	1.90593700	1.23618800	1.50467500
C	4.30021900	-0.26149300	1.54643900
C	2.19823900	0.34763700	0.46497200
C	2.80132300	1.35421700	2.57838600
C	3.96707000	0.59848200	2.61114900
C	3.38203200	-0.38685700	0.48500500
H	1.51460400	0.23512000	-0.36837300
H	2.57765900	2.03131300	3.40012500
H	4.64489300	0.66857900	3.45560700
H	3.57831300	-1.09287400	-0.31513300
N	5.46026100	-1.03018500	1.66965700
C	6.30295600	-1.22821600	0.69817600
C	8.27941600	-1.87486100	-1.31181000
C	7.38096000	-2.18888400	0.95596800
C	6.31394000	-0.55674800	-0.60834400
C	7.24279800	-0.85953900	-1.54048000
C	8.29292200	-2.50856100	0.01487200
H	7.38439900	-2.65001000	1.93882700
H	5.58084800	0.21866400	-0.79944300
H	7.27393300	-0.34997800	-2.49871800
H	9.06833300	-3.24421100	0.21641900
N	9.11402300	-2.12555200	-2.26815300
H	9.78969300	-2.83939100	-1.97778800
S	-4.61012200	-2.81725100	-0.61972900
O	-5.42234300	-4.02218900	-0.69504600
O	-3.33228500	-2.80907000	0.09345400
O	-4.36148600	-2.33941900	-2.15391100
S	0.04304300	3.28499000	-1.29027700
O	1.20897500	2.59464200	-1.84039100
O	0.51667400	4.29630800	-0.11785700
O	-0.85392900	4.03671700	-2.15960300

S-PANI-Zn

C	4.13179400	-0.79675700	-0.33675300
C	6.33235900	0.44577300	0.87429200
C	4.34744300	0.58590300	-0.47896000
C	5.03990100	-1.55148200	0.40960300
C	6.13626900	-0.93062000	1.01273500
C	5.43729600	1.21007500	0.12046900
H	4.89312900	-2.62305600	0.49971100
H	6.84111500	-1.52564200	1.58414000
H	5.59992700	2.27733700	-0.00583400
H	7.18728500	0.92657200	1.33810700
N	3.44023200	1.38938900	-1.34521200
H	2.93314600	0.61836700	-1.94460700
H	3.99398800	2.00177800	-1.95099500
C	2.32894400	2.13023800	-0.71301800
C	-0.11832500	3.13674900	0.11882100
C	1.87629200	3.33732000	-1.23912800
C	1.62086500	1.47258400	0.28424400
C	0.37432700	1.94419700	0.66946600
C	0.65230800	3.85595000	-0.79209700
H	2.43122500	3.87081800	-2.00565700
H	1.98364900	0.55068100	0.72009000
H	0.29522400	4.79704600	-1.20203000
N	-1.48802400	3.61531300	0.45172500
H	-1.63038000	3.45874700	1.46567900
H	-1.54408100	4.62673400	0.27796800
C	-2.61305800	2.86777200	-0.23279700
C	-4.37096300	0.92767700	-1.10583500
C	-2.41498200	2.31326700	-1.49238200
C	-3.77517300	2.63182500	0.50152400
C	-4.67900600	1.67117300	0.04686600
C	-3.32698400	1.36281500	-1.94356700
H	-1.54488000	2.54692900	-2.09575400

H	-3.95281100	3.12095200	1.45536500
H	-5.56733100	1.45422700	0.63012100
H	-3.17335500	0.86195500	-2.89287700
N	-4.88010700	-0.33935200	-1.46739500
C	-4.69517400	-1.33468700	-0.65874500
C	-2.71149500	-3.02003700	0.21963700
C	-4.57461000	-2.67319500	-1.28213100
C	-4.27370300	-1.25897800	0.75693700
C	-3.31261300	-2.09347300	1.18210400
C	-3.58266300	-3.49494600	-0.86137900
H	-5.14656200	-2.87391500	-2.18298100
H	-4.69475000	-0.51553100	1.41979600
H	-2.91798400	-2.05968800	2.19361100
H	-3.32635300	-4.40453100	-1.39742100
N	-1.42800100	-3.28211400	0.30676000
H	-1.10261400	-3.96442700	-0.38035700
S	2.70853500	-1.65171900	-1.06271000
O	2.21130200	-0.68994600	-2.11285100
O	1.71425800	-1.68165600	0.10894800
O	3.09704400	-2.97891200	-1.50342600
S	-0.63413900	0.79293800	1.62972100
O	-1.52116300	1.62672200	2.44880600
O	0.28999100	-0.17233200	2.32238100
O	-1.29341400	-0.04277800	0.54383900
Zn	-0.10716900	-1.80037200	0.83198600

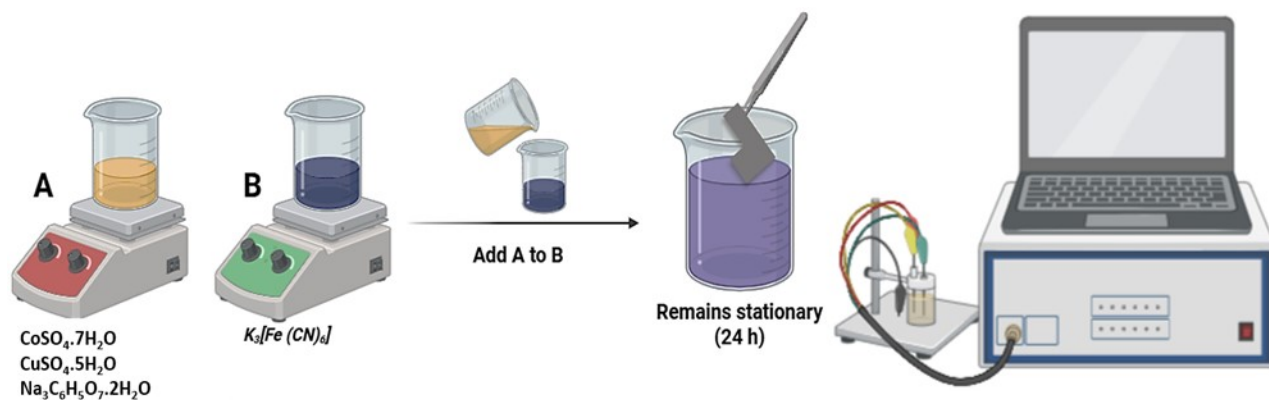


Figure S1. Schematic illustration of the synthesis procedure of PBA

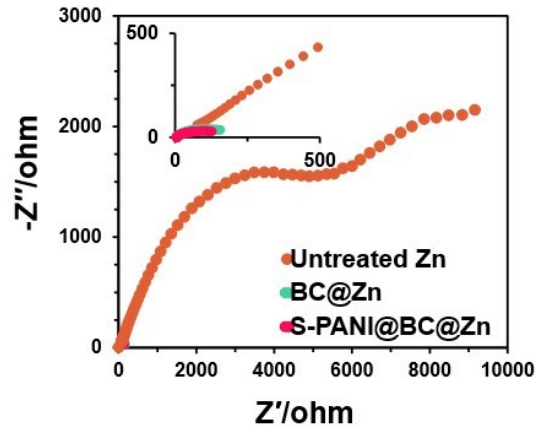


Figure S2. EIS curves of untreated Zn, BC@Zn, and S-PANI@BC@Zn after cycling stability.

Calculation of Texture Coefficient (TC) from XRD Data

We have carried out a quantitative analysis of the XRD data by calculating the RTC values for the major diffraction planes, including (002), (101), and (100). The TC values were obtained using the standard formula:

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{\frac{1}{n} \sum_n I(hkl)/I_0(hkl)}$$

where $I(hkl)$ and $I_0(hkl)$ represent the measured and standard intensity values, respectively. Based on the major Zn diffraction peaks ((002), (100), (101), (102), and (103)), the calculated RTC values reveal a distinct reconfiguration of the Zn growth orientation after surface modification. For the bare Zn electrode, the RTC values are calculated to be RTC (002) = 0.68, RTC (100) = 0.90, RTC (101) = 0.75, RTC (102) = 1.45, and RTC (103) = 1.24, indicating that the pristine Zn surface does not favor basal-plane deposition and instead exhibits relatively disordered crystal growth. In contrast, after introducing the S-PANI@BC interlayer, the crystallographic orientation undergoes a pronounced transition. The calculated RTC values become RTC (002) = 1.31, RTC (100) = 0.81, RTC (101) = 0.32, RTC (102) = 1.45, and RTC (103) = 1.12.

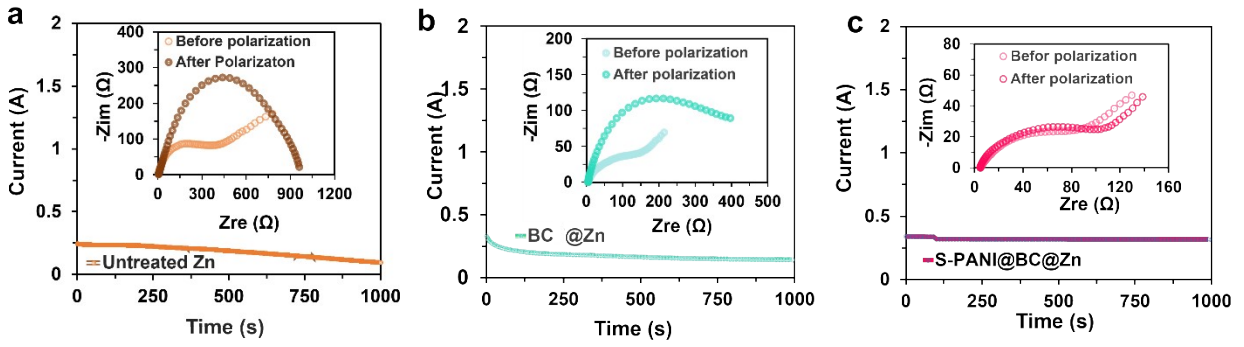


Figure S3. $t_{Zn^{2+}}$ calculation from EIS & CA before and after polarization in Zn||Zn cells. (a) Untreated Zn, (b) BC@Zn, and (c) S-PANI@BC@Zn

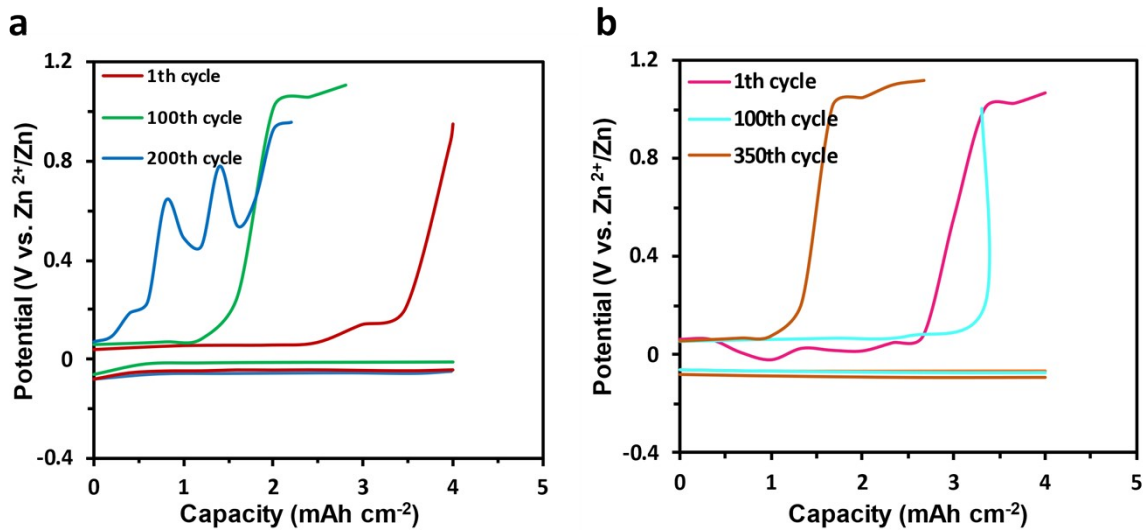


Figure S4. GCD of (a) untreated Zn, and (b) BC@Zn at different cycles at 20 mA cm⁻²/ 4 mAh cm⁻²

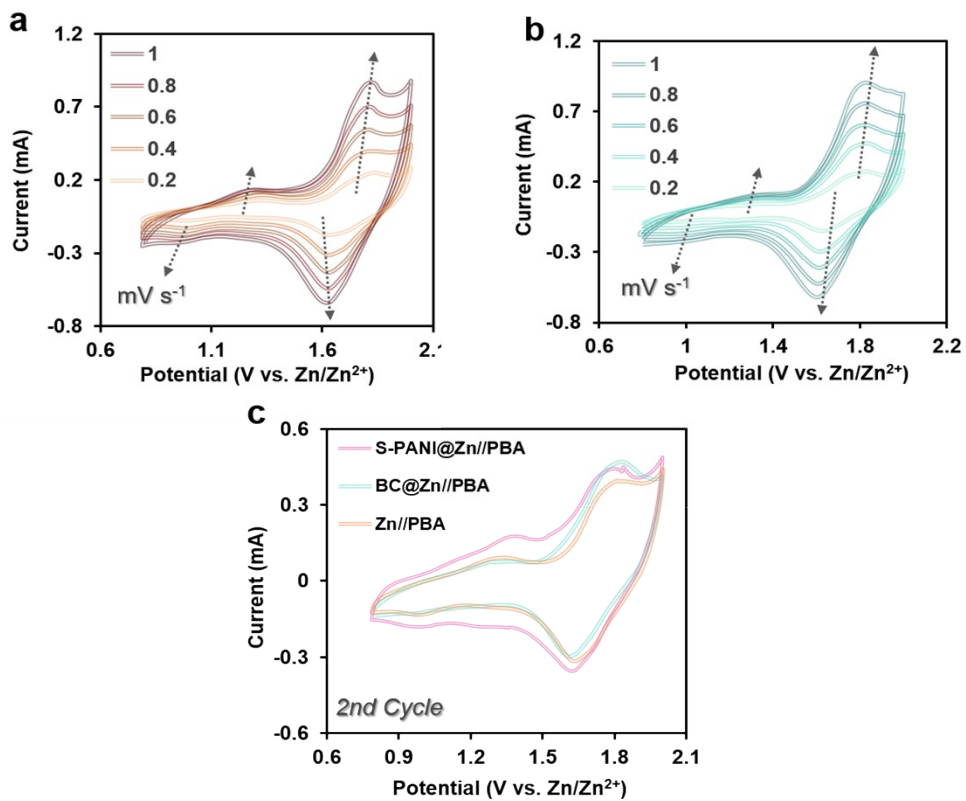


Figure S5. CV profiles of full batteries with PBA cathodes and (a) untreated Zn, and (b) BC@Zn anodes at scan rates from 0.2 to 1.0 mV s⁻¹, and (c) comparison of different anodes with a scan rate of 0.5 mV s⁻¹

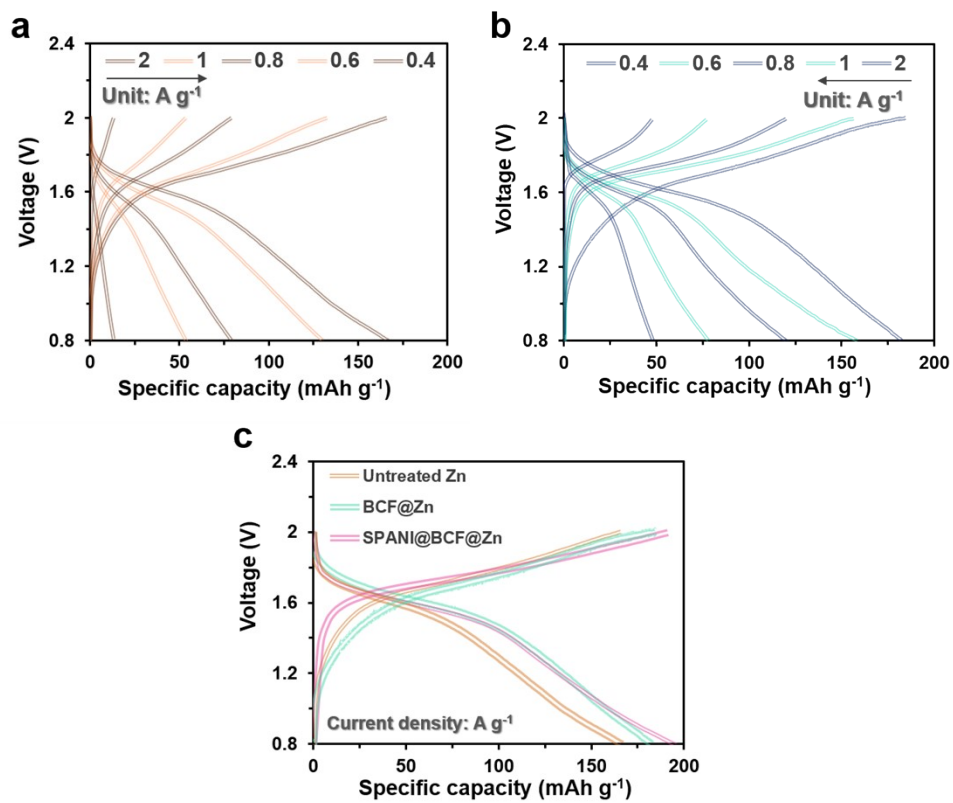


Figure S6. GCD profiles of full batteries with PBA cathodes and (a) untreated Zn, (b) BC@Zn anodes at various current densities, and (c) comparison of different anodes in 0.4 A g⁻¹.

Table S2. Fitted parameters obtained from EIS analysis and equivalent circuit modeling of the different full batteries: a) untreated Zn||PBA, b) BC@Zn||PBA, and c) S-PANI@BC@Zn||PBA.

a				
<u>Element</u>	<u>Freedom</u>	<u>Value</u>	<u>Error</u>	<u>Error %</u>
Rs	Free(+)	4.41	0.42212	9.5719
CPE1-T	Free(+)	0.00066127	4.9462E-05	7.4798
CPE1-P	Free(+)	0.39192	0.0080928	2.0649
Rct	Free(+)	314.7	37.802	12.012
Wo-R	Free(+)	759.2	91.564	12.061
Wo-T	Free(+)	38.16	12.484	32.715
Wo-P	Free(+)	0.31004	0.034676	11.184
Chi-Squared:		0.0001003		
Weighted Sum of Squares:		0.0031093		
b				
<u>Element</u>	<u>Freedom</u>	<u>Value</u>	<u>Error</u>	<u>Error %</u>
Rs	Free(+)	13.65	0.20341	1.4902
CPE1-T	Free(+)	6.4373E-05	3.1084E-06	4.8287
CPE1-P	Free(+)	0.70837	0.0060011	0.84717
Rct	Free(+)	277.4	6.7006	2.4155
Wo-R	Free(+)	507.5	128.66	25.352
Wo-T	Free(+)	25.62	16.899	65.96
Wo-P	Free(+)	0.42317	0.027	6.3804
Chi-Squared:		0.0006815		
Weighted Sum of Squares:		0.021127		
c				
<u>Element</u>	<u>Freedom</u>	<u>Value</u>	<u>Error</u>	<u>Error %</u>
Rs	Free(+)	7.776	0.12603	1.6208
CPE1-T	Free(+)	0.00024829	1.3627E-05	5.4883
CPE1-P	Free(+)	0.61817	0.006652	1.0761
Rct	Free(+)	148.3	6.484	4.3722
Wo-R	Free(+)	1314	1.513E05	11514
Wo-T	Free(+)	426	1.3E05	30516
Wo-P	Free(+)	0.37709	0.021424	5.6814
Chi-Squared:		0.00038625		
Weighted Sum of Squares:		0.011974		

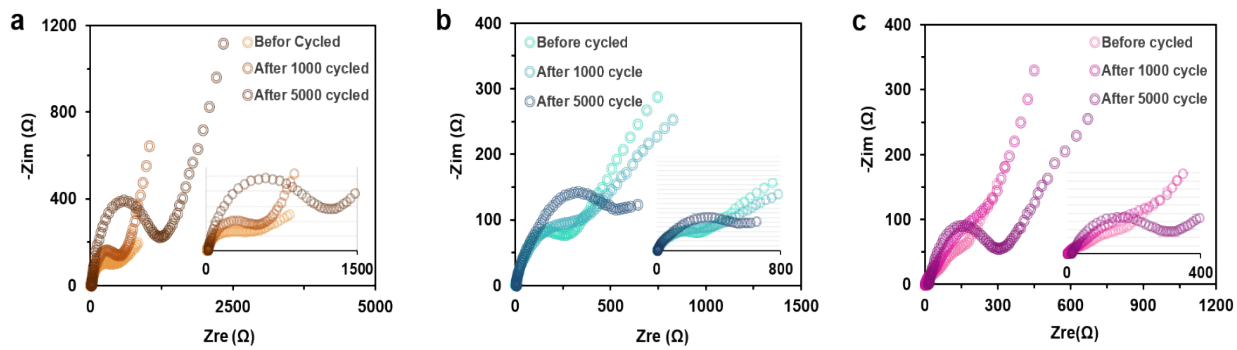


Figure S7. Nyquist plot of various full batteries before and after long-term cycle life examination. (a) untreated Zn||PBA, (b) BC@Zn||PBA, and (c) S-PANI@BC@Zn||PBA.

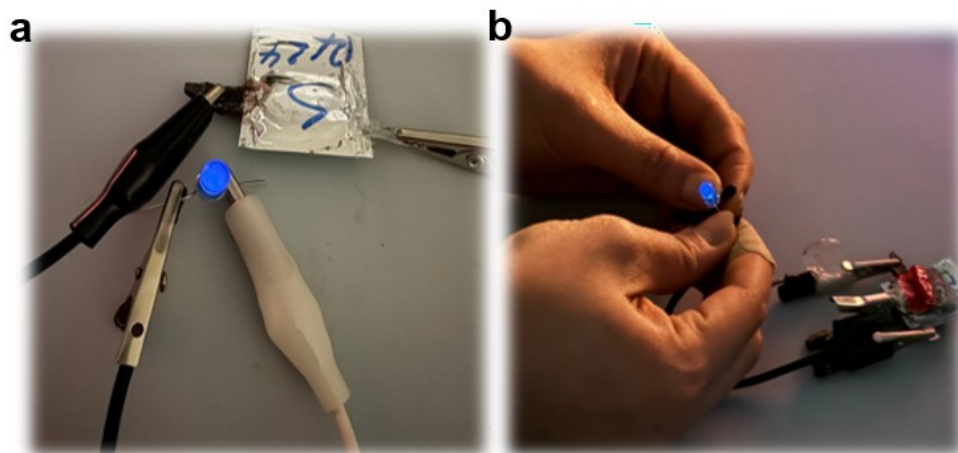


Figure S8. Evaluation of full cell ability in lighting up a blue light-emitting diode. (a) before and (b) after 5000 charge/discharge cycles.

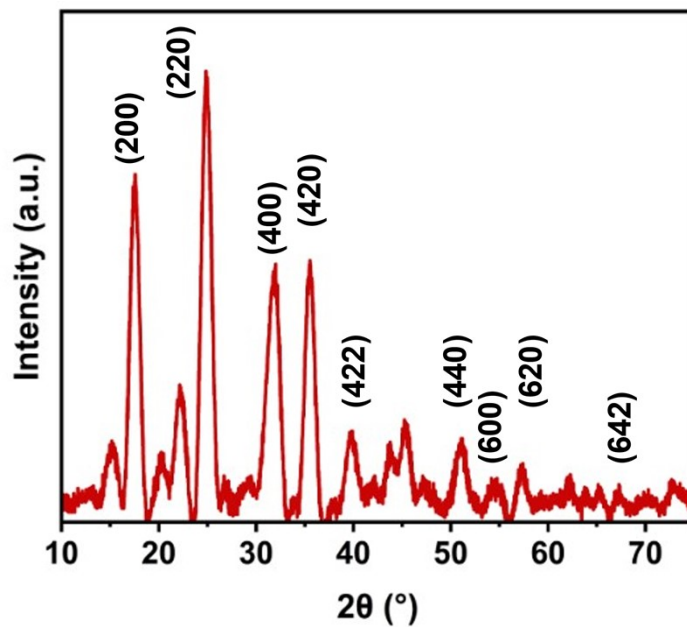


Figure S9. XRD pattern of PBA.

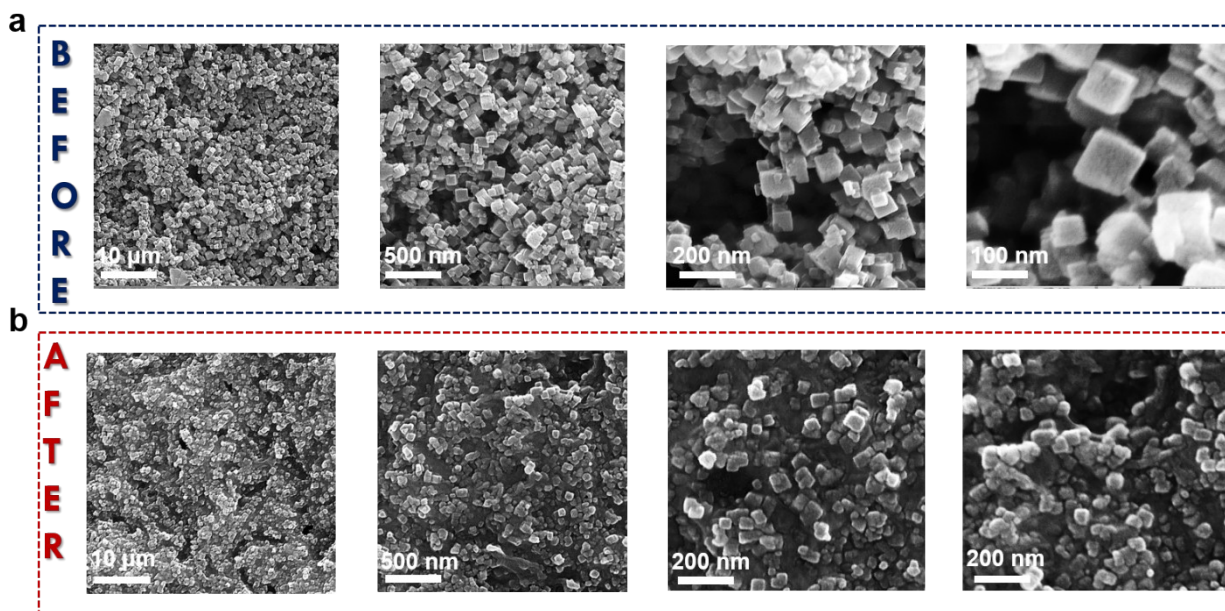


Figure S10. FE-SEM images of electroactive PBA after 5000 cycles