Supplementary Information

Super-Resolved Dynamics of Isolated Zinc Formation during Extremely Fast Electrochemical Deposition/Dissolution Processes

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Supplementary material and methods

Materials

The materials used included zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, 99.995%, Shanghai Macklin Biochemical), polyethyleneimine ($(CH_2CH_2NH)_n$, 99%, Shanghai Macklin Biochemical), zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$, 98%, Shanghai Macklin Biochemical), hydrogen peroxide (H_2O_2, 30%, analytical grade, YongHua Chemical), sulfuric acid (H_2SO_4, 1 M, AR, Shenzhen Chemical Technology), deionized (DI) water (Shanghai Titan Technology), and a platinum wire electrode (Φ 0.5 mm, Tianjin Eilian).

Magnetron sputtering was performed to deposit a copper film with a thickness of 400 nm on a clean glass coverslip. Copper was used as the current collector owing to its stability and low price. A perforated polydimethylsiloxane membrane (pore diameter: 2 mm), with a thickness of 100 μm, was used to define the geometry/as the upper sheath of the ring electrode. A mixed solution of 0.5 M H_2SO_4 and 30% H_2O_2 (ratio of 1:1) was used to etch the unprotected area, resulting in a nanoscale ring electrode with a diameter of approximately 2.1 mm. The copper ring electrode was used as the working electrode, and a platinum wire electrode was used as both counter and reference electrodes. The electrode area can be calculated according to the following formula:

$$S_{Electrode} = \pi dh$$

where S is area of working electrode, d is the diameter of nanoscale ring electrode, h is the thickness of copper film. Therefore, the electrode area was 2.6 x 10^{-5} cm^2. The zinc electrochemical deposition and dissolution process were at current of 1, 2, and 5 μA. Accordingly, the current densities were 38, 76, and 189 mA/cm^2, corresponding to rates of 38, 76, and 189 C in a zinc-ion coin cell with an area capacity of 1 mAh/cm^2.

Operando Super-resolution Imaging

A microscope (ECLIPSE Ti2-E, Nikon) with an oil immersion objective (CFI Apochromat TIRF 60XC, Nikon, numerical aperture of 1.49), sCMOS camera (Zyla 4.2, Andor), and electrochemical workstation (V46840, Ivium) was used for imaging. A commercially available phase ring device was used to relay the back focal plane (BFP) to the other conjugate positions in the microscope; a diaphragm was installed on the relayed BFP to block the light reflected from the metal electrode as well as the other totally reflected light. This ensured that only the light scattered from the sample passed through, thus physically separating the reflected light from the light scattered from the dendrites. The experiment was performed with a Perfect Focus System (PFS) from Nikon. The PFS could automatically correct focus drift by detecting and tracking the position of the coverslip surface in real time. A high-speed camera was used with the phase ring device and diaphragm to obtain super-resolution images, that is, images with nanoscale and millisecond resolutions. Simultaneously, the electrochemical signals were recorded using an electrochemical workstation. The laser wavelength was 488 nm, laser power was 10 mW, incident angle was 70°, and exposure time was 2 ms. The imaging process has no delay and the framerate is 498.4 fps with an Andor Zyla

sCMOS Camera in 16-bit recording mode. The full width imaged is in 700 pixel x 200 pixel or 75.83 μm x 21.67 μm.

The ThunderSTORM plugin of the ImageJ software was used to achieve super-resolution localization. The recording was duplicated into two subrecordings that emphasized the difference in i-Zn growth (an interval of 160 ms was suitable in this case). The localization results were visualized using ThunderSTORM with an integrated Gaussian rendering. Next, temporal color-coded super-resolution images were obtained by processing the ThunderSTORM results using the Temporal-Color Code plugin in ImageJ.

***Ex-Situ* Characterization**

The morphology of the passivation layer was observed using an HIM system (ORION NanoFab, Zeiss). The electrolyte was removed immediately after the completion of the dissolution process. The electrode area was rinsed twice with DI water, and the remaining solution was aspirated. After all the model battery tests were completed, the slide was rinsed with water and isopropanol and then dried thoroughly. The composition of passivated products was determined using XPS (PHI 5000 Versaprobe III, ULVAC-PHI, Inc.). A monochromatic Al-Kα X-ray source was used. The standard used for data calibration was the C1s peak at 284.8 eV. The processing steps for the slides were the same as those used before characterization using HIM.

Supplementary figures

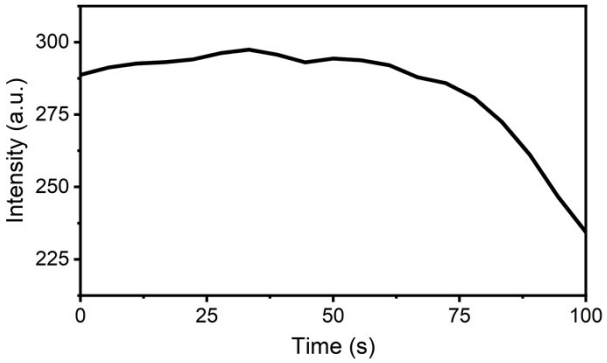

Figure S1. Intensity–time curve of isolated zinc and dendrites in TIRDF recording of zinc dendrites dissolution process with 1M $ZnSO_4$ electrolyte at a discharging current density of 76 mA/cm^2 in a zinc air model battery. The dendrites had been deposited at 76 mA/cm^2 and 300 μC (deposition time of 150 s).

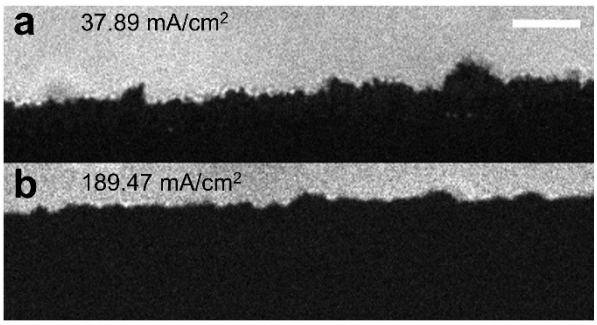

Figure S2. Final BF images of the dendrites deposition process with 1M $ZnSO_4$ electrolyte at charging current densities of (a) 38 mA/cm^2 and (b) 189 mA/cm^2. Scale bar: 5 μm.

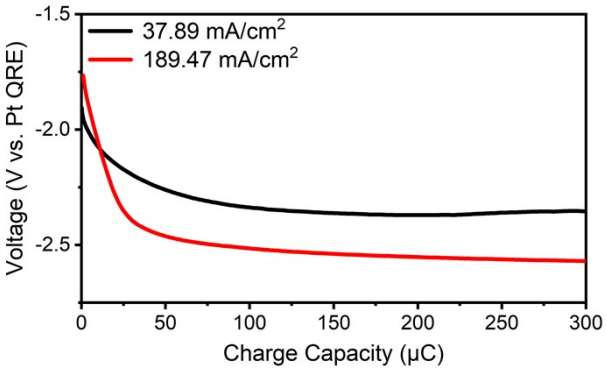

Figure S3. Galvanostatic deposition curves of zinc dendrites with 1M $ZnSO_4$ electrolyte at charging current densities of 38 mA/cm^2 (black) and 189 mA/cm^2 (red) in a zinc air model battery.

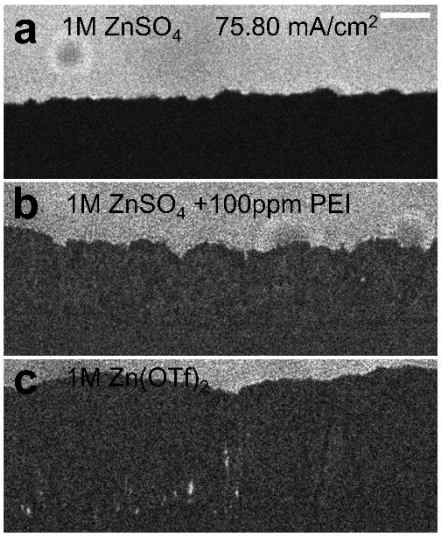

Figure S4. Final BF images of the dendrites deposition process using (a) 1M $ZnSO_4$, (b) 1M $ZnSO_4$ + 100ppm PEI, and (c) 1M $Zn(OTf)_2$ as electrolytes at a charging current density of 76 mA/cm^2 and 300 μC (deposition time of 150 s). Scale bar: 5 μm.

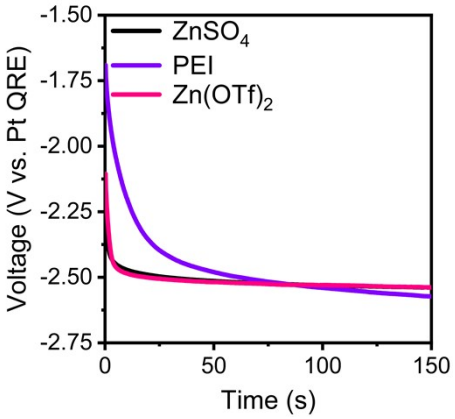

Figure S5. Galvanostatic deposition curves of the zinc dendrites using 1M $ZnSO_4$ (black), 1M $ZnSO_4$ + 100ppm PEI (purple), and 1M $Zn(OTf)_2$ (magenta) as electrolytes at a charging current density of 76 mA/cm^2 and 300 μC in a zinc air model battery.

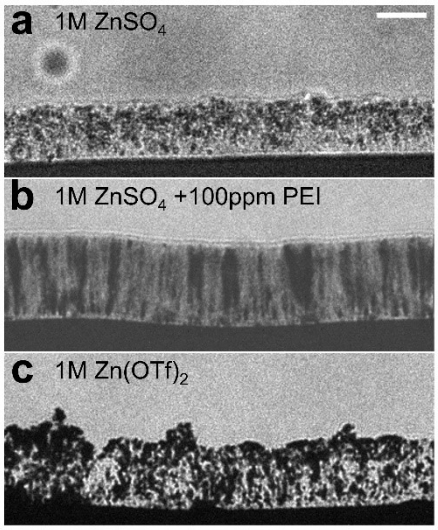

Figure S6. Final BF images of the dendrites dissolution process using (a) 1M $ZnSO_4$, (b) 1M $ZnSO_4$ + 100ppm PEI, and (c) 1M $Zn(OTf)_2$ as electrolytes at a discharging current density of 189 mA/cm^2. The zinc dendrites had been deposited at 189 mA/cm^2 and 300 μC (deposition time of 60 s). Scale bar: 5 μm.

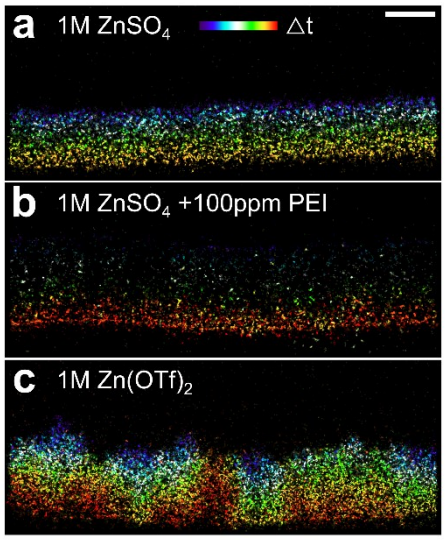

Figure S7. Temporal color-coded super-resolution images of the dendrites dissolution process using (a) 1M $ZnSO_4$, (b) 1M $ZnSO_4$ + 100ppm PEI, and (c) 1M $Zn(OTf)_2$ as electrolytes at a discharging current density of 189 mA/cm^2. The zinc dendrites had been deposited at 189 mA/cm^2 and 300 μC (deposition time of 60 s). Scale bar: 5 μm.

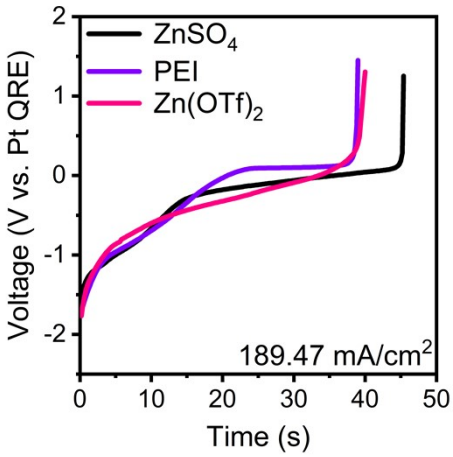

Figure S8. Galvanostatic dissolution curves of zinc dendrites using 1M $ZnSO_4$ (black), 1M $ZnSO_4$ + 100ppm PEI (purple), and 1M $Zn(OTf)_2$ (magenta) as electrolytes at a discharging current density of 189 mA/cm^2 in a zinc air model battery. The dendrites had been deposited at charging current density of 189 mA/cm^2 and 300 μC (deposition time of 60 s).

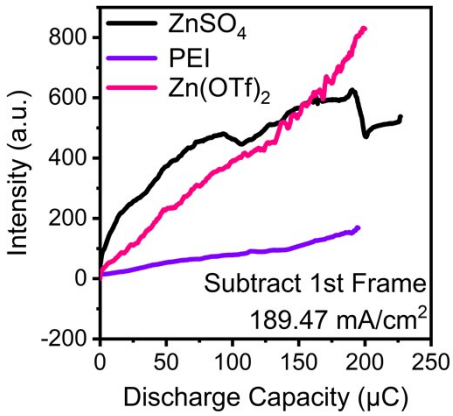

Figure S9. Scattering intensity–discharge capacity curves obtained from processed TIRDF recording by subtracting first image using 1M $ZnSO_4$ (black), 1M $ZnSO_4$ + 100ppm PEI (purple), and 1M $Zn(OTf)_2$ (magenta) as electrolytes at a discharging current density of 189 mA/cm^2 in a zinc air model battery. The dendrites had been deposited at charging current density of 189 mA/cm^2 and 300 μC (deposition time of 60 s).

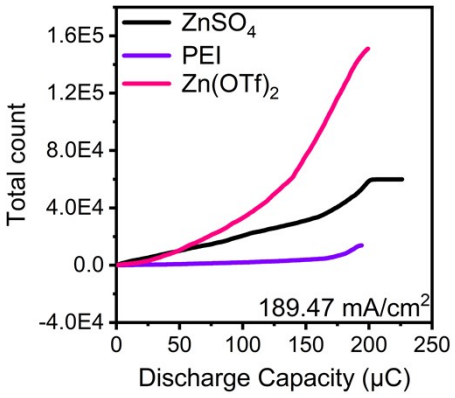

Figure S10. Total count–discharge capacity curves of microscopic and nanoscopic orphaning using 1M $ZnSO_4$ (black), 1M $ZnSO_4$ + 100ppm PEI (purple), and 1M $Zn(OTf)_2$ (magenta) as electrolytes at a discharging current density of 189 mA/cm^2 in a zinc air model battery. The dendrites had been deposited at charging current density of 189 mA/cm^2 and 300 μC (deposition time of 60 s).