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Supporting Information

To what extent do anions affect the electrodeposition of Zn?

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Experimental

Materials:

All Zn salts $ZnCl_2$, $Zn(ClO_4)_2$, and $ZnSO_4$ were purchased from Alfa Aesar. Grafoil sheets of 25 μM were used as a current collector for the Zn deposition, and 25 μM Zn sheets were used as counter and reference electrodes. Both sheets were purchased from Sigma Aldrich.

Methods:

Electrochemical analyses were performed on a VMP-3 instrument, in a 2-electrode configuration, (both for the T-cells and Fluded cells) where Graphol was working and Zn was used as the counter-reference electrode. For the Teflon T-cell configuration, a 200μm thick glassy fiber separators were used. All Zn electrolyte solutions were prepared by adding the specific Zn salt to a known volume of double distiled water. The mass of the salt was calculated to the molar mass of the salt, and the volume of water to form a 1M solution.

Multi-harmonic quartz-crystal measurements using EQCM-D were done with a Q-Sense E1 module (QCM-D from Biolinve Scientific) at overtone orders from 1st to 13th (all overtones are measured within 1 sec). Ti/Au-coated AT-cut 5 MHz quartz crystal (AWSensors) was cleaned in Piranha solution, rinsed in water, and dried under N_2 gas flow. In all EQCM-D experiments, the temperature was kept constant at 25 °C. QSoft401 software was used for Data acquisition. The in-situ electrochemistry measurements were conducted using a BioLogic SP-300 potentiostat.

HR-SEM imaging was performed using a Magellan XHR 400L FE-SEM (FEI Company) equipped with an EDS detector (Oxford Instruments). XRD measurements were performed using an AXS D8 ADVANCE diffractometer (Bruker Inc., Germany) using Cu Ka radiation, a Ni filter, and a scintillation counter. XPS spectra were acquired on a Physical Electronics Versa Probe 5000 (ULVAC-PHI, Inc., Japan) spectrometer using Al-Kα monochromatic X-rays of 100 μm. Raman spectra were recorded with a Renishaw Raman InVia Confocal Microscope (U.K.) with the 532 nm laser, 1200 gr/mm grating, and 100× lens was used with 10% laser power.

Classical molecular dynamics simulation

Molecular dynamics (MD) simulations were carried out using the package LAMMPS[1]]. Zn^{2+} parameters were taken from ref [[2]. Anion parameters were taken from ref [3] for Cl^-, ref [4]] for ClO_4^{-}, and ref [5] for SO_4^{2-}. The SPC/fw model [[6]] was used to describe water. The partial charges of ions were scaled by a constant of 0.8 to approximate the effect of charge transfer and polarizability in the bulk phase.[[7] The long-range electrostatic interactions were calculated using the particle-particle particle-mesh (PPPM) method [[8]] with a real space cutoff of 12 Å. The same cutoff was used for van der Waals interactions and a tail correction was applied.

The simulation boxes were built up by placing the proper numbers (see Table S1) of Zn^{2+} salts and water molecules randomly in a cubic box using the package Packmol[9,10] For the liquid bulk simulations, the systems were equilibrated for 2 ns in the isothermal-isobaric (NPT) ensemble followed by production simulations of 10 ns in the canonical ensemble (NVT). All the simulations were carried out at 298 K. The Nosé-Hoover thermostat [11] and the extended Lagrangian approach[[12] were applied to control the temperature and pressure, respectively. A time constant of 100 fs was used in both the thermostat and barostat. The pressure was fixed at one atmosphere in all constant pressure simulations with isotropic volume fluctuations.

The double-layer structure of electrolytes was examined in MD simulations where electrolytes were sandwiched between two electrodes that consisted of three graphene layers each. The cross-section of the graphene has a dimension of 31.9286 Å×34.0320 Å and the distance between adjacent graphene layers was set to 3.35Å. The equilibrated bulk simulation boxes were deformed gradually during a 10 ns NVT simulation so that the final dimensions in the X and Y directions match the graphene cross-section. At the end of this step, the Z dimension of the electrolyte box was found to be ~120 Å for each system. The electrolyte was put between two electrodes and the Z dimension was allowed to equilibrate for 2 ns with X and Y dimensions fixed. During this equilibration step, positions of the electrode atoms were fixed relative to each other while each electrode was allowed to move as a whole along the Z-direction. Once the system was equilibrated, the positions of the electrodes were fixed and MD simulations were performed for 400 ns in the NVT. For these systems, the periodic boundary conditions were applied in X and Y directions and a vacuum space three times of the liquid phase was added in the Z-direction. The slab-slab interaction was removed. No tail correction was applied to van der Waals interactions. To describe the interaction between the electrode carbon atoms and the electrolytes, the van der Waals parameters σ and ε for these carbon atoms are 3.40Å and 0.1093 kcal/mol, respectively. To mimic a charged electrode, static partial charges were added to the carbon atoms in the first layer of each electrode (with direct contact with electrolytes), positive on one side and negative on the other so that the whole system is charge neutral.

Table S1. Composition of simulation boxes for 1 M Zn^{2+} aqueous electrolytes.

	Number of salt molecules	Number of water molecules
$ZnCl_2$	75	3937
$Zn(ClO_4)_2$	75	3911
$ZnSO_4$	75	4109

Results

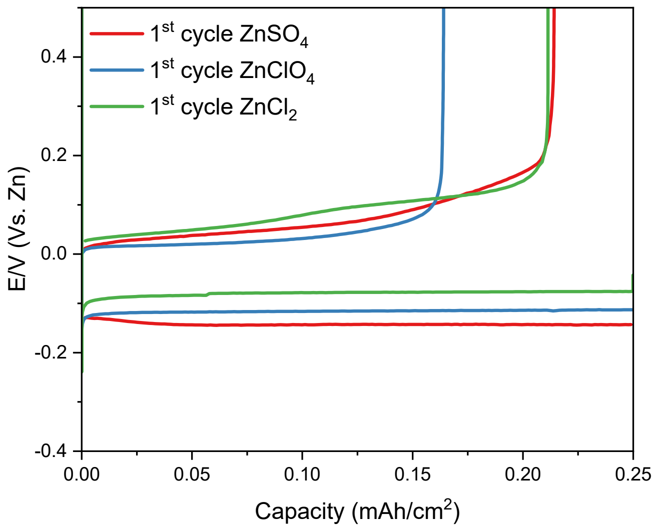

Figure S1. 1st cycle obtained at 0.5A/g in all the examined Zn-anions solutions

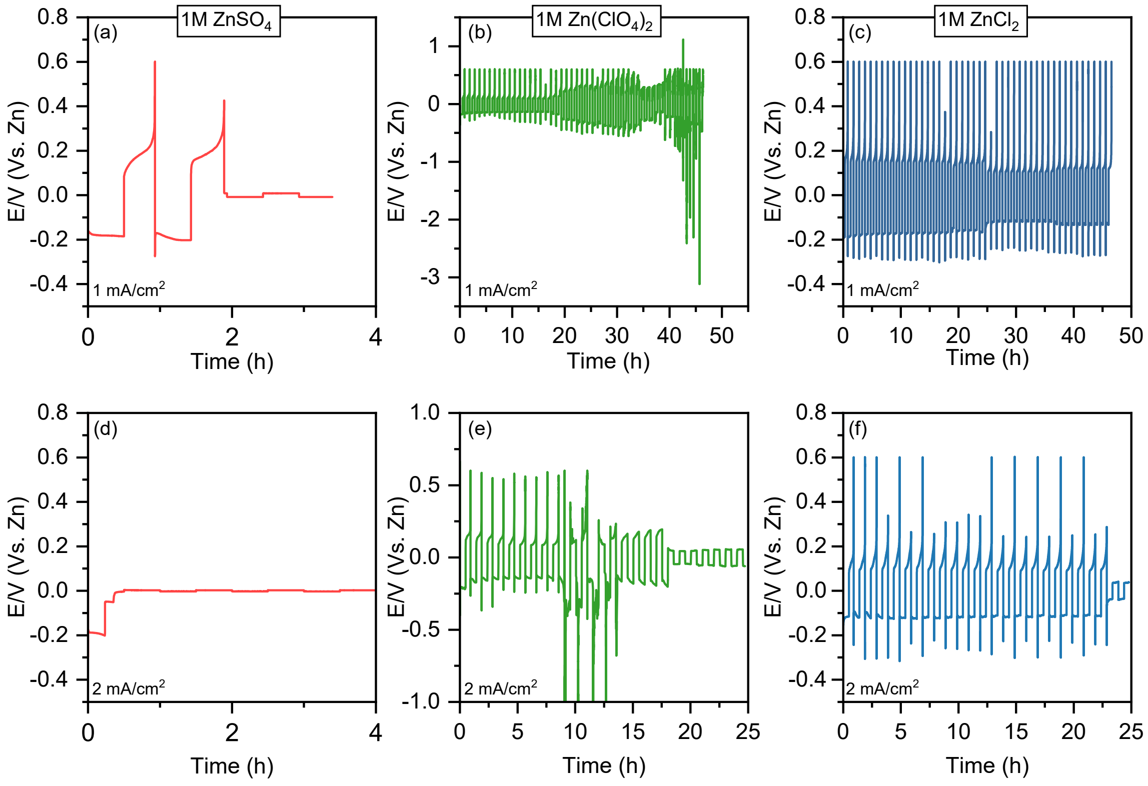

Figure S2 Voltage vs. time profile of SO4, $(ClO_4)_2$ and Cl_2 in current densities of $1mA/cm^2$ (a-c) and $2mA/cm^2$

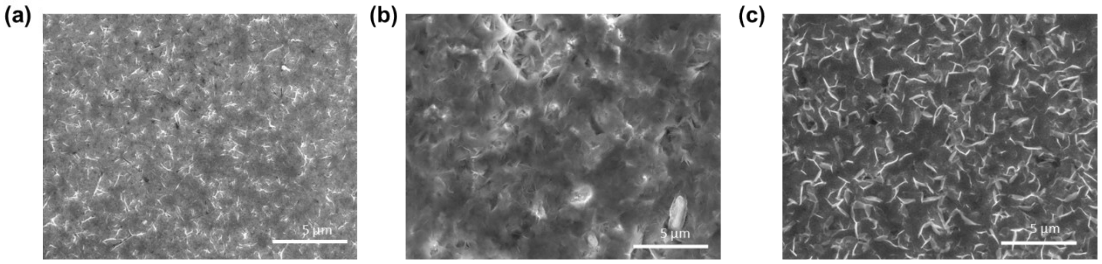

Figure S3. SEM images of the Au quartz sensors after electrodeposition of Zn metal in EQCM-D cells containing 1M (a) $ZnCl_2$ (b) $Zn(ClO_4)_2$ and (c) $ZnSO_4$ electrolyte solutions.

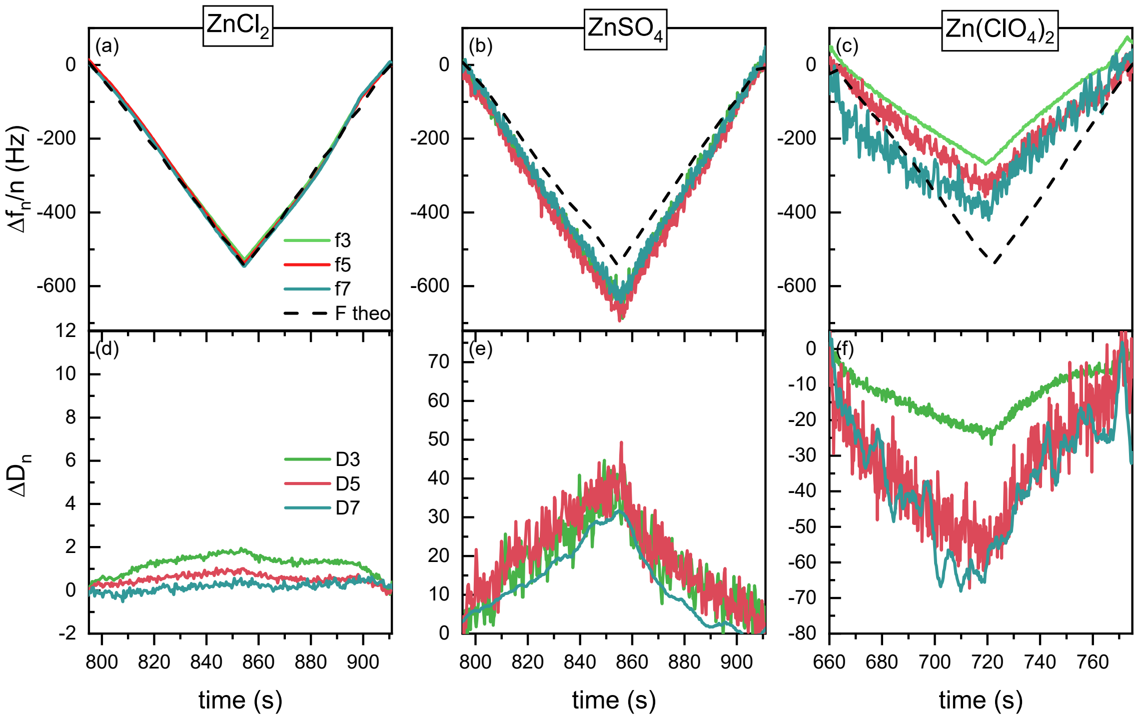

Figure S4. An enlarged image of the multi-harmonic frequency and dissipation responses from EQCM-D measurements that are presented in Figure 3 (main manuscript).

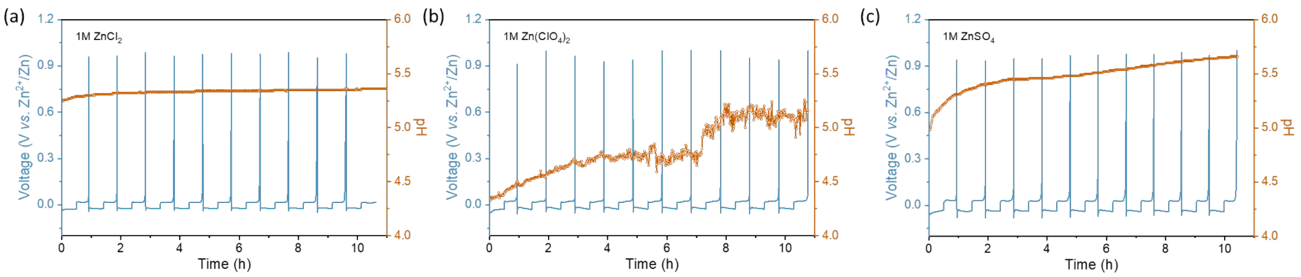

Figure S5. Variations in pH values during reversible Zn electrodeposition cycling in cells containing 1M (a) $ZnSO_4$ (b) $Zn(ClO_4)_2$ and (c) $ZnCl_2$ electrolyte solutions.

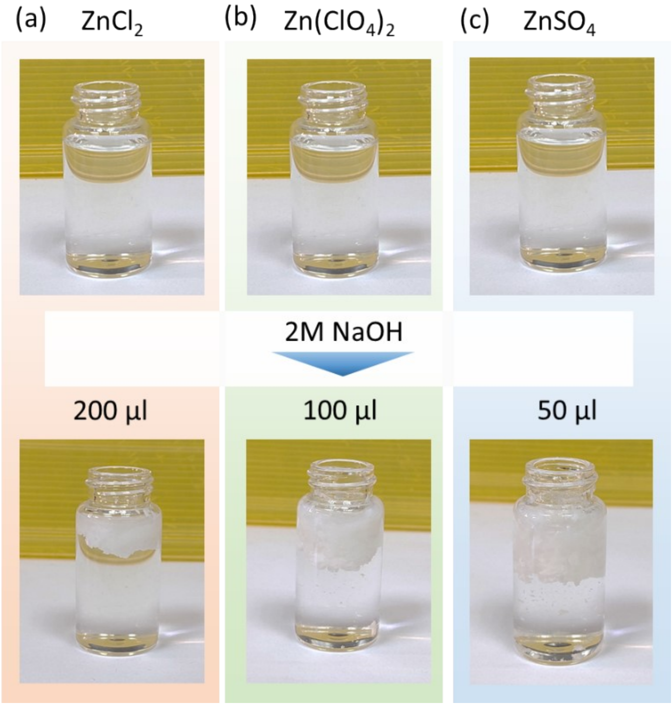

Figure S6. Titration results of 20ml Zn electrolytes by 2M NaOH: **(a)** ZnCl, **(b)** $Zn(ClO_4)_2$ and **(c)** $ZnSO_4$

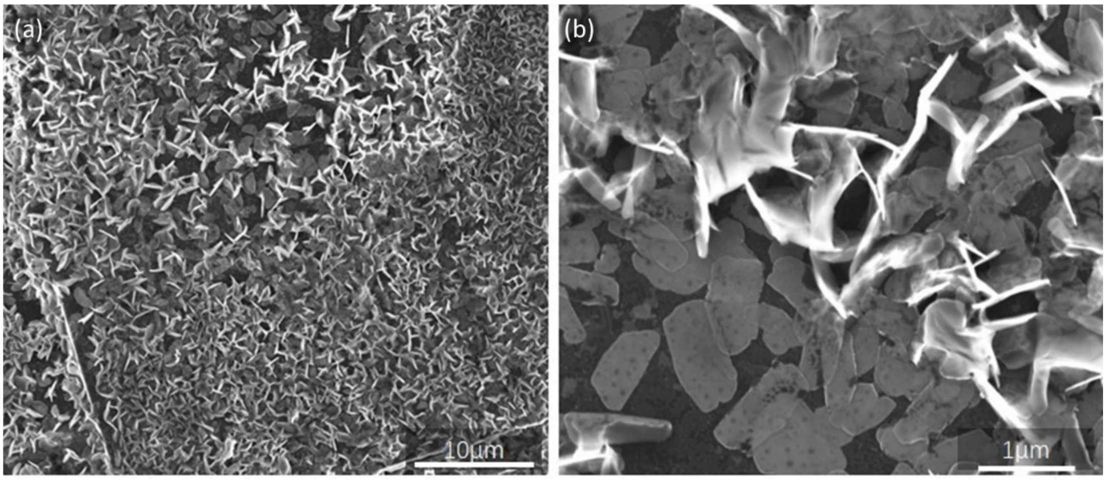

Figure S7 Formation of vertically originated Zn flakes in 1M $ZnSO_4$

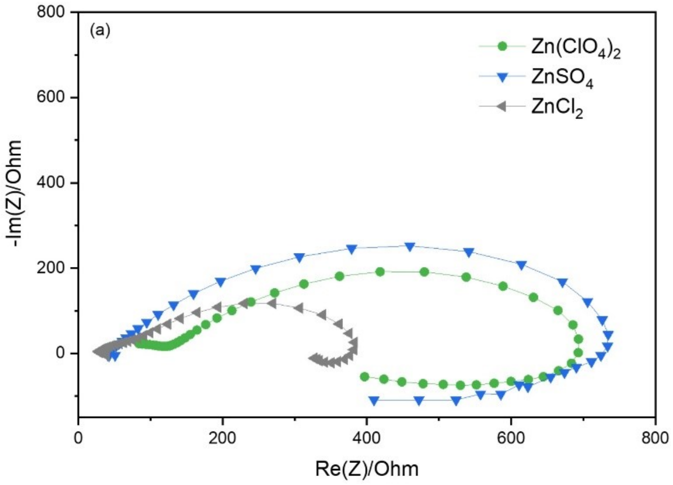

Figure S8. Electrochemical impedance spectroscopy measurements after the first and tenth Zn electrodeposition process on Cu substrates in different Zn-based aqueous solutions.

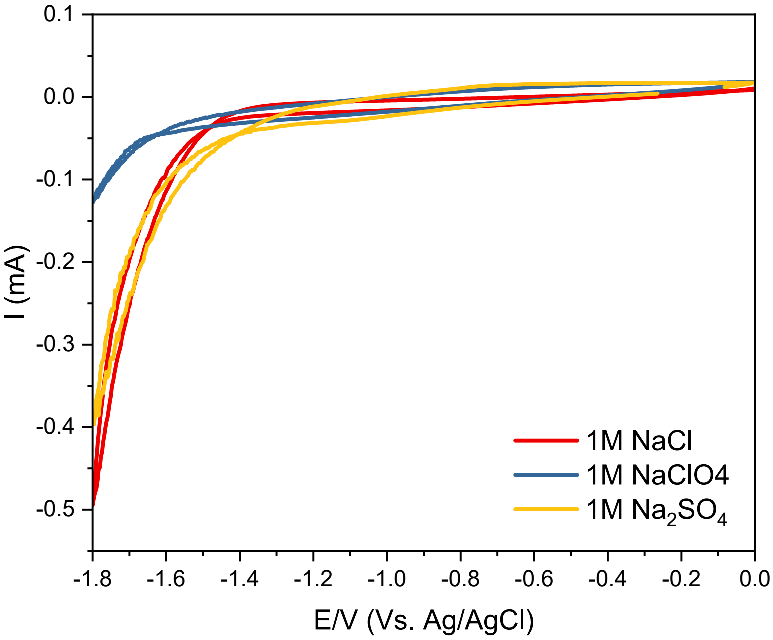

Figure S9 Electrochemical stability window of Zn electrodes in various aqueous solutions. Cyclic voltammograms were taken at a scan rate of 5 mV·s.

Referances:

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