Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information for

Sodium Succinate as Functional Electrolyte Additive to Achieve Highly Reversible Zinc-Ion Batteries

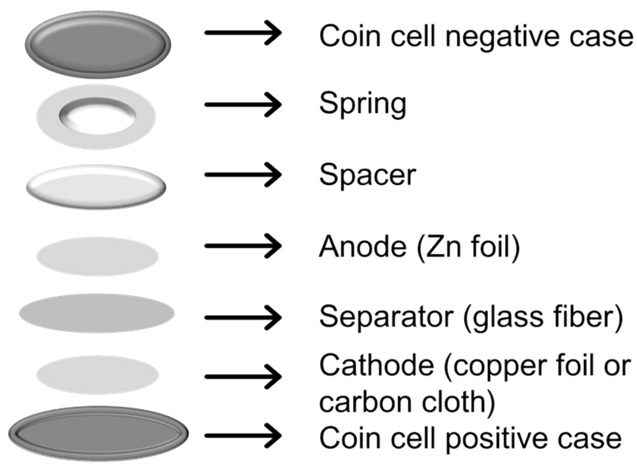


Figure S1. Cell configuration.

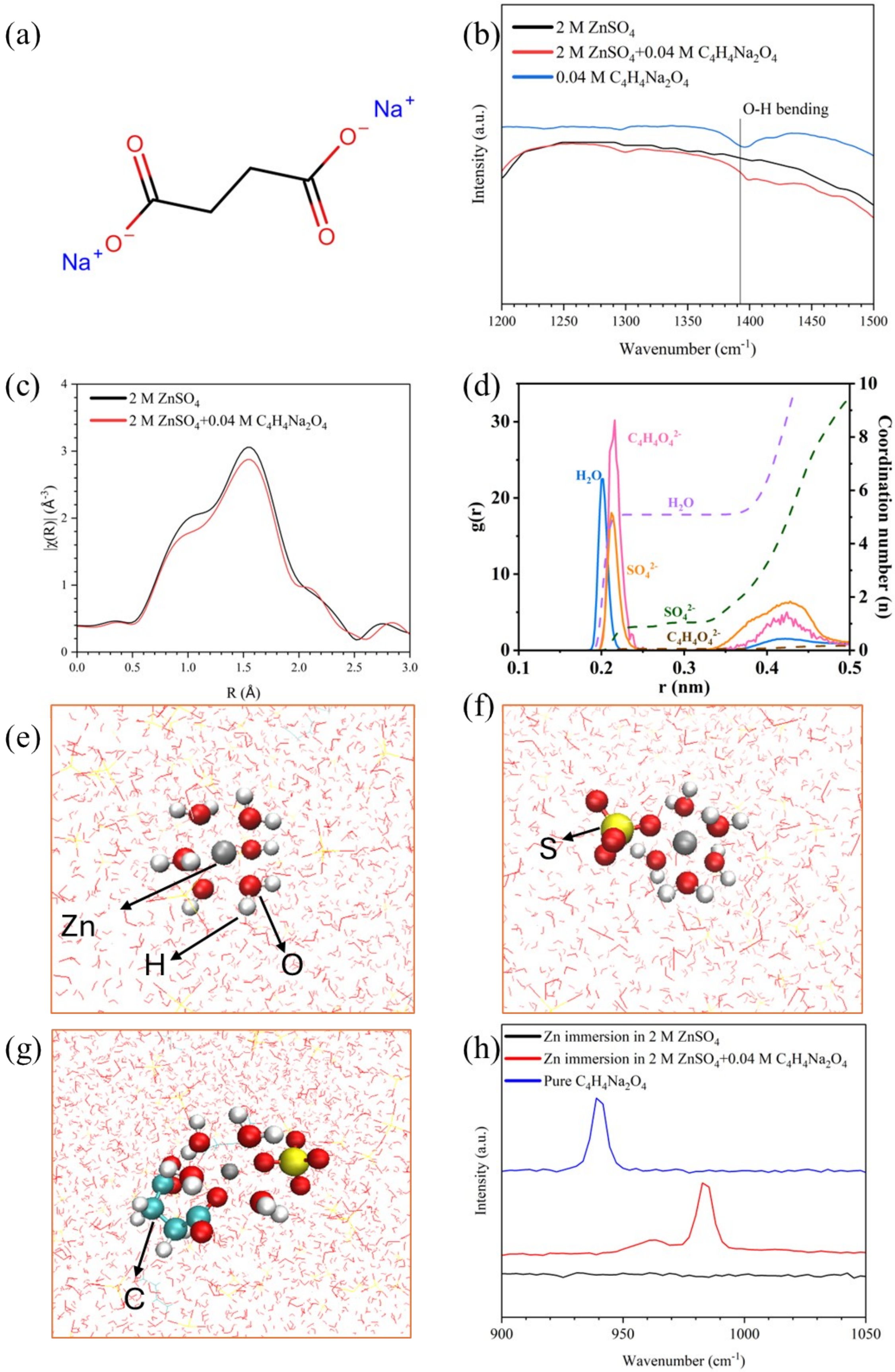
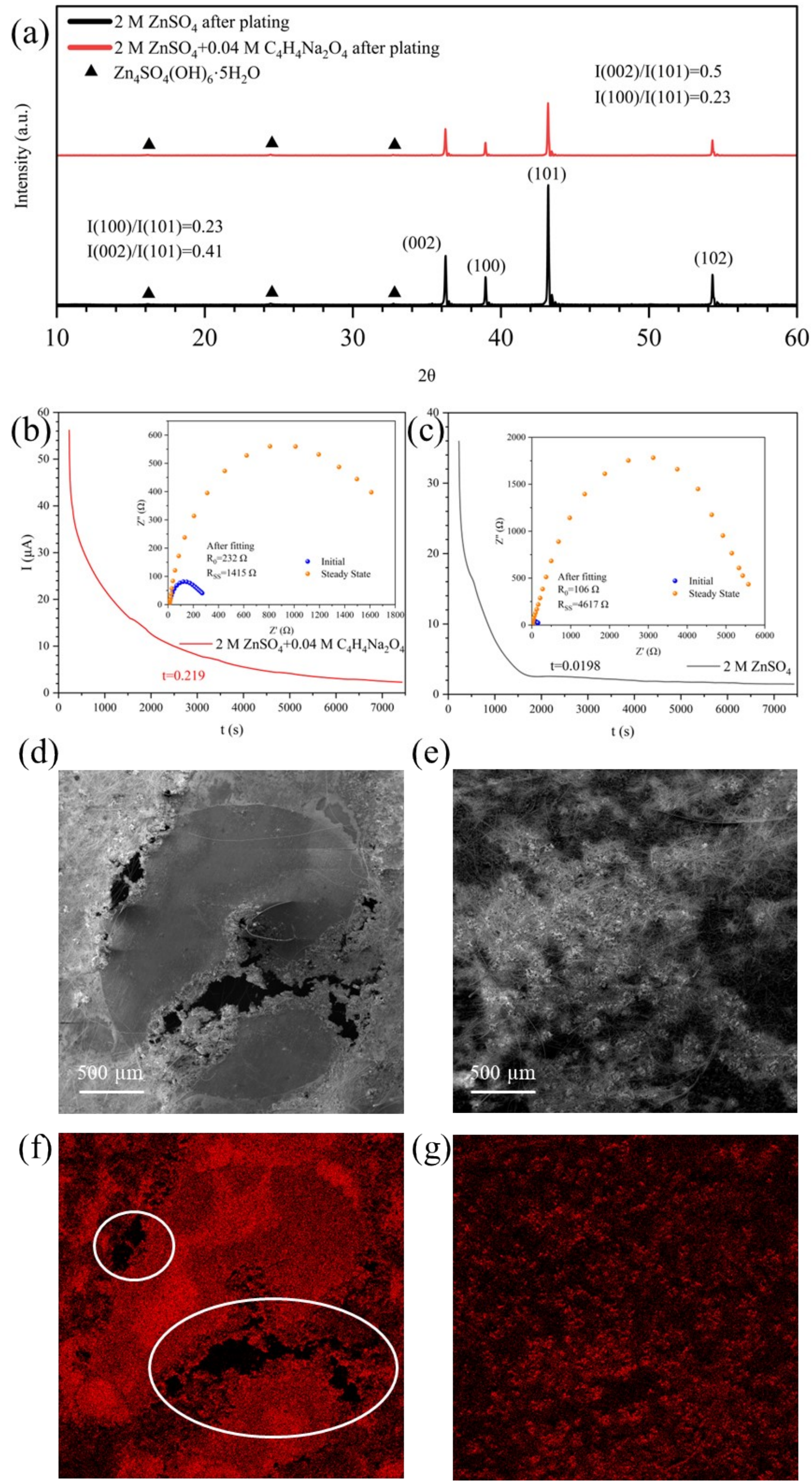

(a)
Na+
O−
O
O
O−
Na+
(b)
2 M ZnSO4
2 M ZnSO4+0.04 M C4H4Na2O4
0.04 M C4H4Na2O4
O-H bending
Intensity (a.u.)
Wavenumber (cm-1)
1200
1250
1300
1350
1400
1450
1500
(c)
2 M ZnSO4
2 M ZnSO4+0.04 M C4H4Na2O4
|χ(R)| (Å-3)
R (Å)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
1
2
3
4
(d)
C4H4O4 2-
H2O
H2O
SO4 2-
SO4 2-
C4H4O4 2-
g(r)
Coordination number (n)
r (nm)
0.1
0.2
0.3
0.4
0.5
0
10
20
30
0
2
4
6
8
10
(e)
Zn
H
O
(f)
S
(g)
C
(h)
Zn immersion in 2 M ZnSO4
Zn immersion in 2 M ZnSO4+0.04 M C4H4Na2O4
Pure C4H4Na2O4
Intensity (a.u.)
Wavenumber (cm-1)
900
950
1000
1050

Figure S2. (a) Chemical structure of sodium succinate. (b) Raman spectra for zinc foils immersed in different electrolytes and pure sodium succinate. (c) Processed EXAFS results for electrolytes with and without sodium succinate. (d) Simulated radial distribution functions (RDFs) for $ZnSO_4$ electrolyte with succinate molecules. Distribution of H_2O molecules in the first hydration layer of the Zn^{2+}, without (e)-(f) and with (g) succinate molecules. (h) Fourier-transform infrared (FTIR) spectra for different solutions.



(a)
2 M $ZnSO_4$ after plating
2 M $ZnSO_4$+0.04 M $C_4H_4Na_2O_4$ after plating
$Zn_4SO_4(OH)_6 \cdot 5H_2O$
I(002)/I(101)=0.5
I(100)/I(101)=0.23
Intensity (a.u.)
(101)
I(100)/I(101)=0.23
I(002)/I(101)=0.41
(002)
(100)
(102)
10
20
30
40
50
60
2θ
(b)
I (μA)
After fitting
R_0=232 Ω
R_{SS}=1415 Ω
Initial
Steady State
Z'' (Ω)
Z' (Ω)
2 M $ZnSO_4$+0.04 M $C_4H_4Na_2O_4$
t=0.219
t (s)
(c)
After fitting
R_0=106 Ω
R_{SS}=4617 Ω
Initial
Steady State
Z'' (Ω)
Z' (Ω)
t=0.0198
2 M $ZnSO_4$
t (s)
(d)
500 μm
(e)
500 μm
(f)
(g)

Figure S3. (a) XRD patterns from Zn electrodes after cycling in different electrolytes at 2 mA cm^{-2} and 2 mAh cm^{-2} for 200 cycles with the last reaction being the plating reaction (PDF#039-0688 for $Zn_4SO_4(OH)_6{\cdot}5H_2O$). Chronoamperometry curves obtained using (b) 2 M $ZnSO_4$+0.04 M SS and (c) 2 M $ZnSO_4$ with the corresponding electrochemical impedance spectra presented as insets. SEM SE images of Zn foil after cycling using (d) 2 M $ZnSO_4$ and (e) 2 M $ZnSO_4$+0.04 M SS. Zn EDX maps of Zn foils after cycling in (f) 2 M $ZnSO_4$ and (g) 2 M $ZnSO_4$+0.04 M SS.

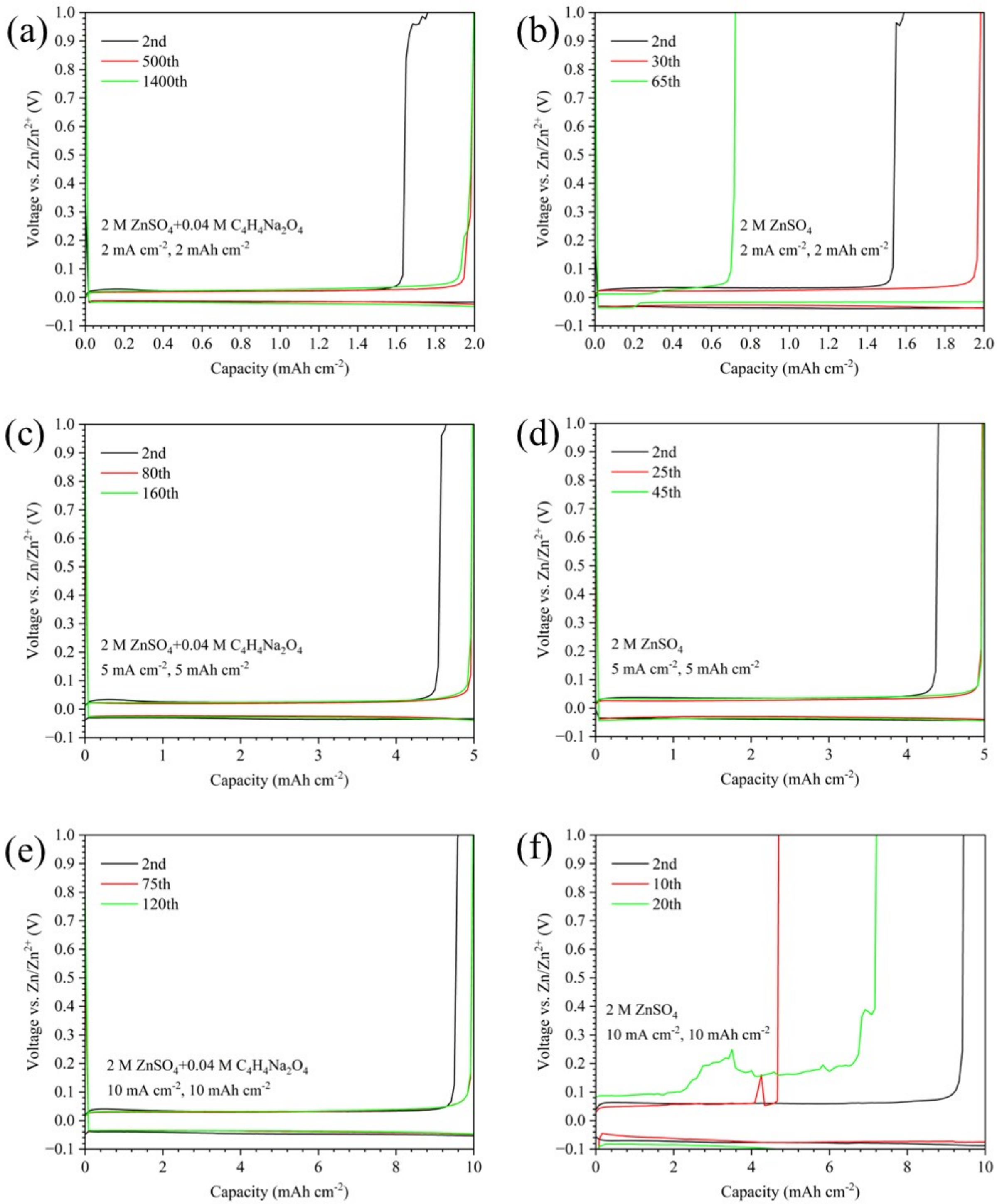


Figure S4. Voltage profiles for Zn||Cu cells with electrolytes containing 0.04 M SS or no SS at current densities ranging from 2 mA cm^{-2} to 10 mA cm^{-2} and capacities ranging from 2 mAh cm^{-2} to 10 mAh cm^{-2}.

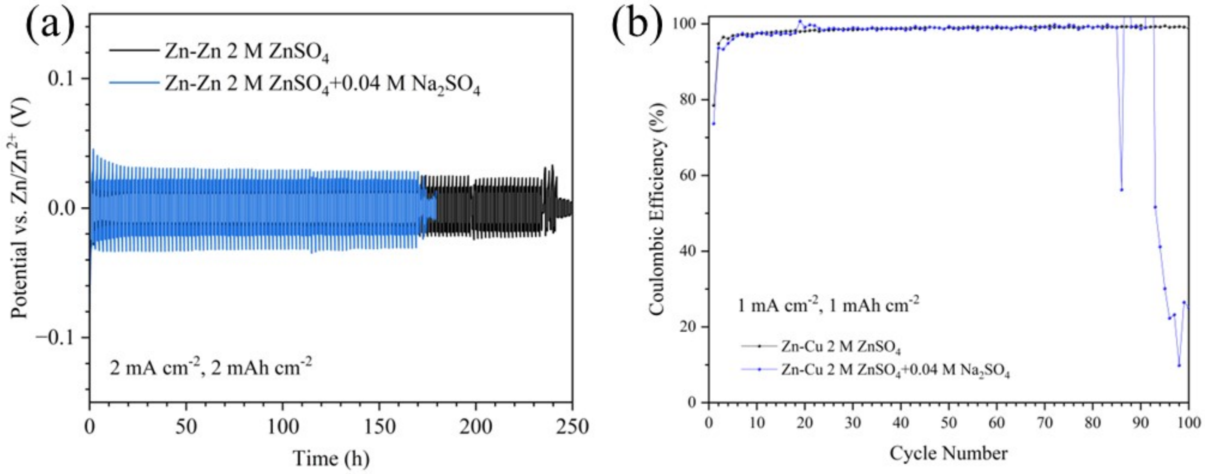


Figure S5. (a) Zn||Zn extended cycling tests at 2 mA cm^{-2} and 2 mAh cm^{-2} using 250 μm Zn foils. (b) Zn||Cu long cycling tests at 1 mA cm^{-2} and 1 mAh cm^{-2} with different electrolytes.

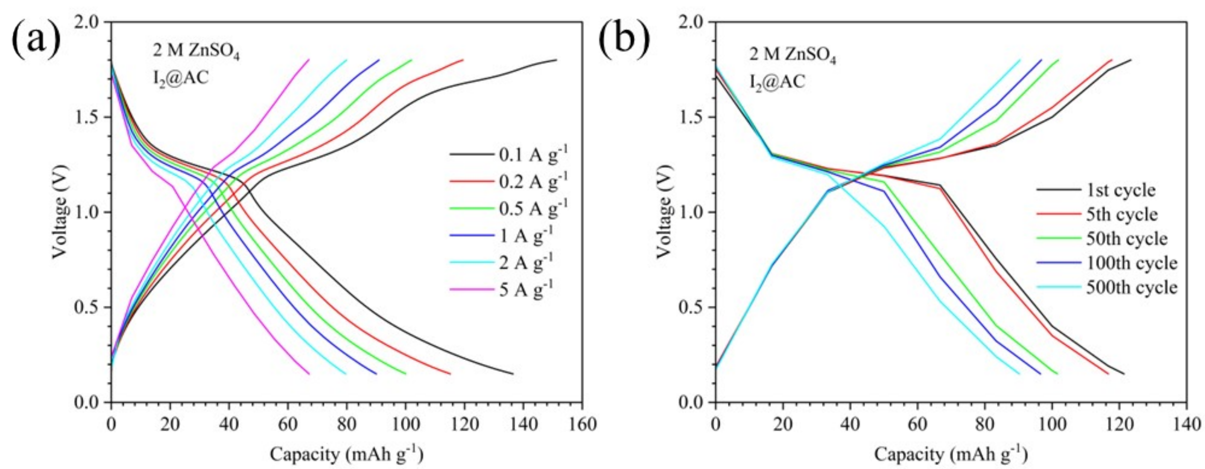


Figure S6. (a) Rate tests and (b) long duration cycling (2 A g^{-1}) charge and discharge profiles of Zn//I_2@AC full cells in $ZnSO_4$.

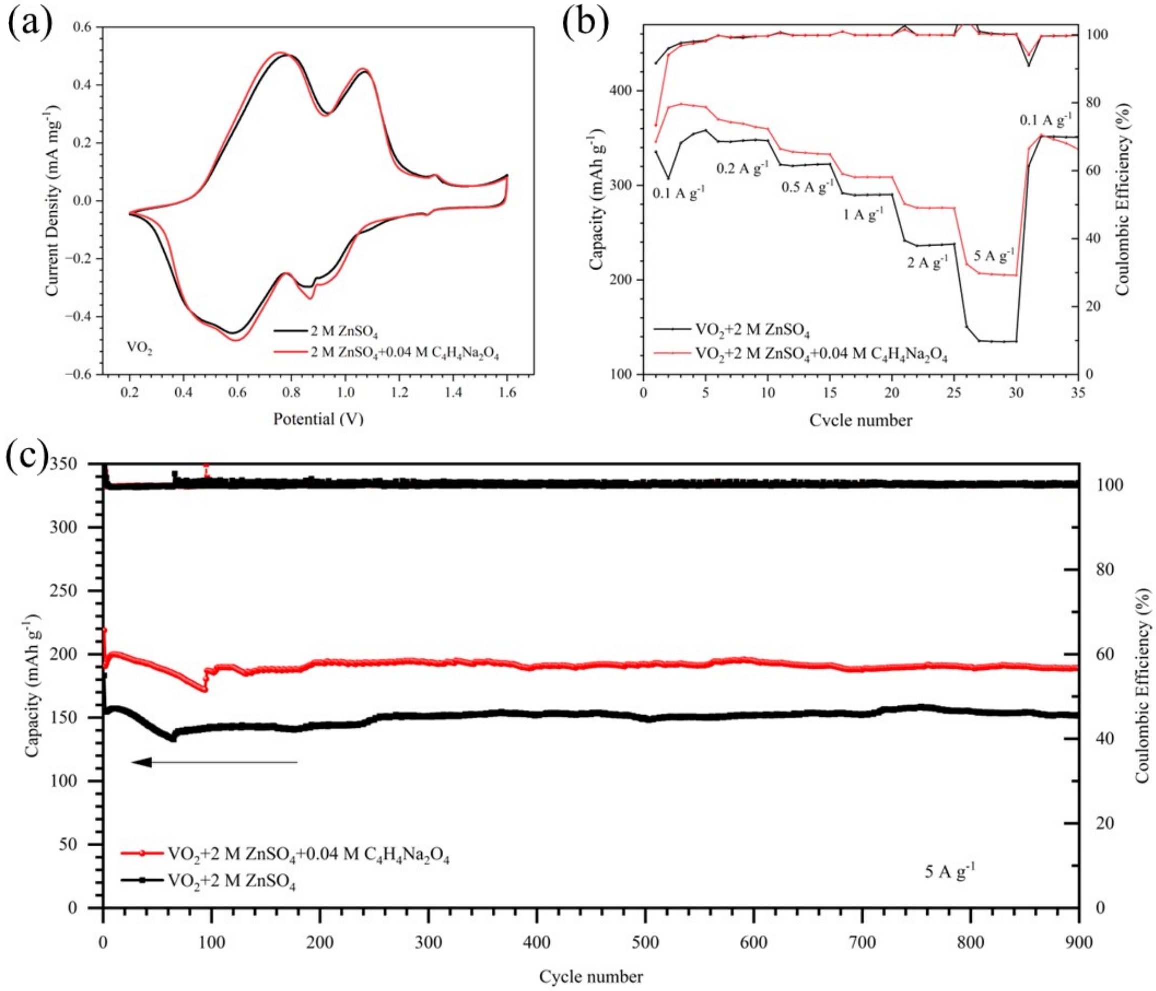


Figure S7. (a) Cyclic voltammetry results obtained from Zn//VO_2 full cells in 2 M $ZnSO_4$ and 2 M $ZnSO_4$ with 0.04 M SS. (b) Zn//VO_2 full cell rate tests. (c) Zn//VO_2 full cell long duration cycling tests at 5 A g^{-1}.

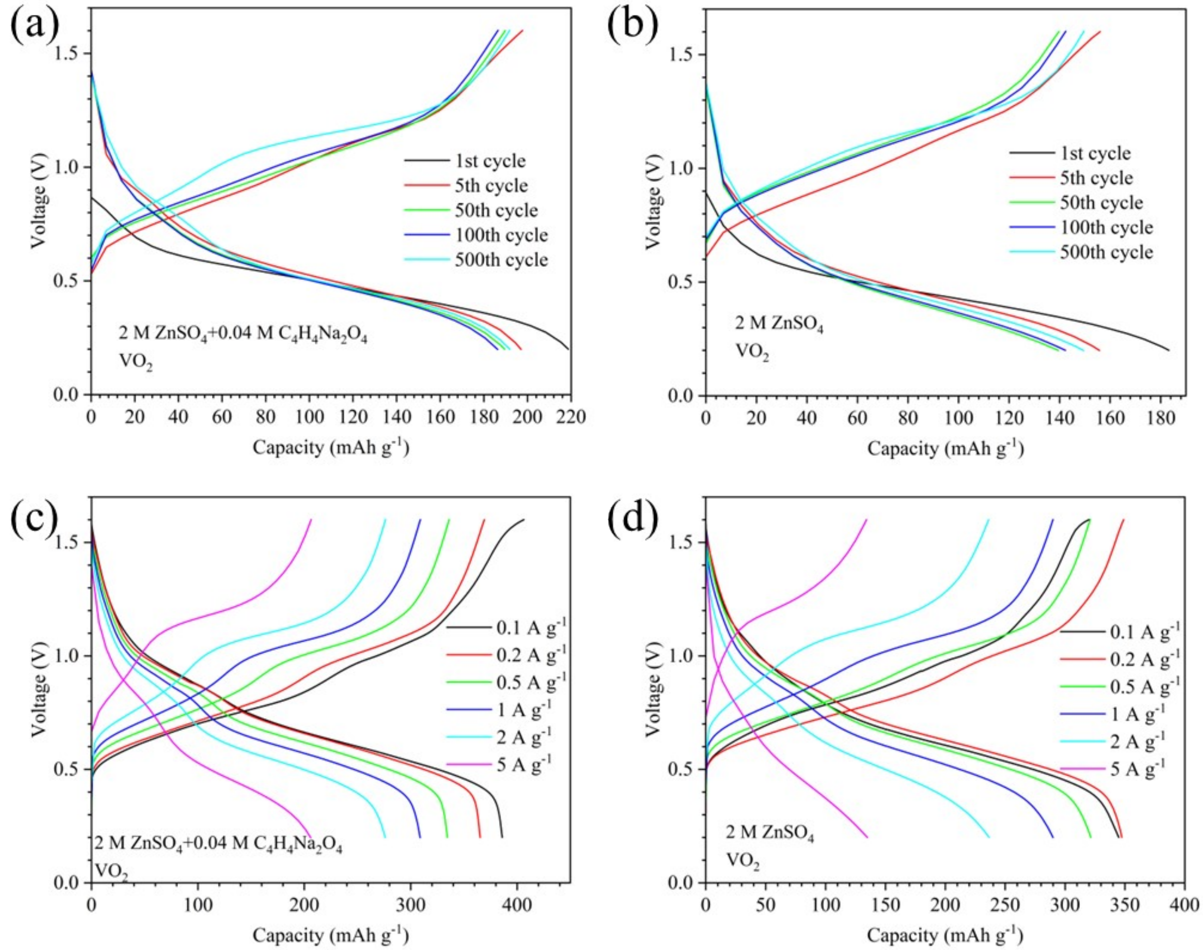


Figure S8. Long duration cycling (5 A g^{-1}) charge and discharge profiles of Zn//VO_2 full cells in (a) 0.04 M SS+2 M $ZnSO_4$ and (b) 2 M $ZnSO_4$. Rate test charge and discharge profiles of Zn//VO_2 full cells in (c) 0.04 M SS+2 M $ZnSO_4$ and (d) 2 M $ZnSO_4$.

Depth of discharge (DOD) was calculated from Equation (1).

$$DOD = \frac{It}{mM} \times 100\% \# (1)$$

where I is the applied current (mA), t is the discharge time (h), m is the mass (m= 21.2 mg for a 30 µm Zn foil) of the zinc anode (g), and M is the theoretical specific capacity of zinc (820 mAh g^{-1}).

SS coverage on Zn surface calculation:

Size of the Zn electrode: 1.13 cm^2

Distance (obtained from simulation) between atoms in the SS molecule:

O^--O^-≈ 5.14 Å; C=O≈ 1.27 Å

Assumptions:

- Additive molecules attach to the Zn surface vertically.
- Additive molecules are considered to be cylindrical with the end of O^- attaching to the Zn surface (height was not considered; i.e., the distance between O^--O^-).
- The working diameter is equal to the diameter of the molecule.
- The radius of the molecule is 1 Å.

Area of each additive molecule:

$$\pi r^2 = \pi \cdot 10^{-16}\ cm^2$$

A hexagonal packing arrangement provides the highest density packing of circles.

The area of the hexagon (assuming the side length of the hexagon is 2r):

$$A = \frac{3\sqrt{3}}{2}(2r)^2 = 6\sqrt{3}r^2$$

Area of circles within the hexagon (each hexagon fits 3 circles):

$$3\pi r^2$$

Maximum packing density for circles in a plane:

$$\frac{3\pi r^2}{\frac{12\sqrt{3}}{2}r^2} = 0.907$$

Number of additive molecules needed to fully cover the Zn surface per unit area (per cm^2):

$$N = \frac{0.907}{\pi \cdot 10^{-16}\, cm^2} = 2.88 \times 10^{15}$$

Number of additive molecules available:

0.04 M was determined as the optimum concentration and 80 μL of electrolyte was used in each cell.

$$N = 0.04\frac{mole}{L} \times 80 \times 10^{-6}\, L \times 6.022 \times 10^{23}\, mole^{-1} = 1.9 \times 10^{18}$$

Number of additive molecules available per cm:

$$N = \frac{1.9 \times 10^{18}}{1.13\, cm^2} = 1.68 \times 10^{18}\, cm^{-2}$$