Supplementary Information

High specific capacity $FeFe(CN)_6$ as the cathode materials in aqueous rechargeable zinc-sodium hybrid batteries

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Table S1. Elemental contents of $FeFe(CN)_6$ sample.

Methods	ICP-OES		Elemental analysis		TG
Elements	K	Fe	C	N	H_2O
Weight %	0	39.64	20.31	24.21	15.84

$FeFe(CN)_6$ Synthesis Reaction:

The reaction of $K_3Fe(CN)_6$ and $FeCl_3 \cdot 6H_2O$ to form $FeFe(CN)_6$ is given below:

$$K_3Fe(CN)_6 + FeCl_3 \cdot 6H_2O \rightarrow FeFe(CN)_6\downarrow + 3KCl + 6H_2O \qquad (S1)$$

Side Reaction: Fe^{2+} and $Fe^{II}(CN)_5^{3-}$ Formation

$$Fe^{3+} + Fe^{III}(CN)_6^{3-} + 2H_2O \rightarrow Fe^{2+} + Fe^{II}(CN)_5^{3-} + NH_4^{+} + CO_2 \qquad (S2)$$

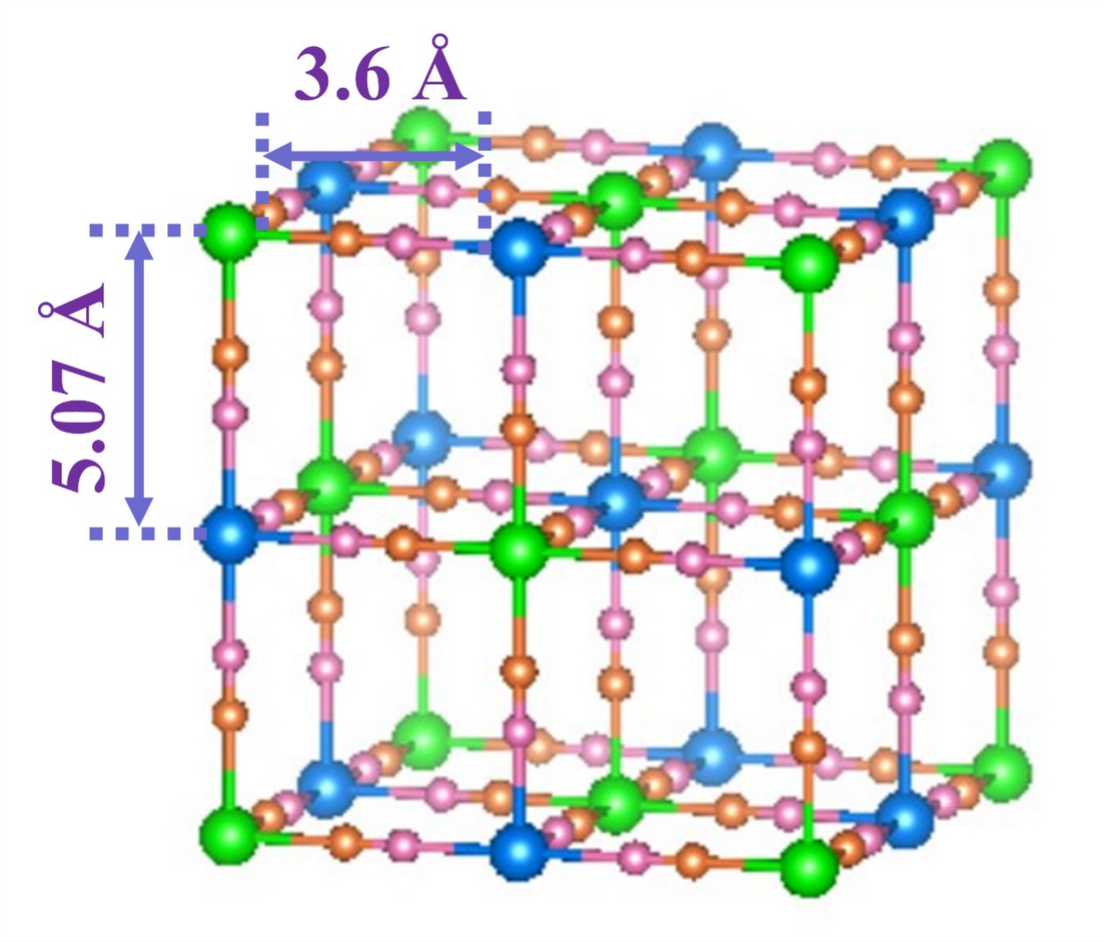

Fig. S1. The structure of $FeFe(CN)_6$.

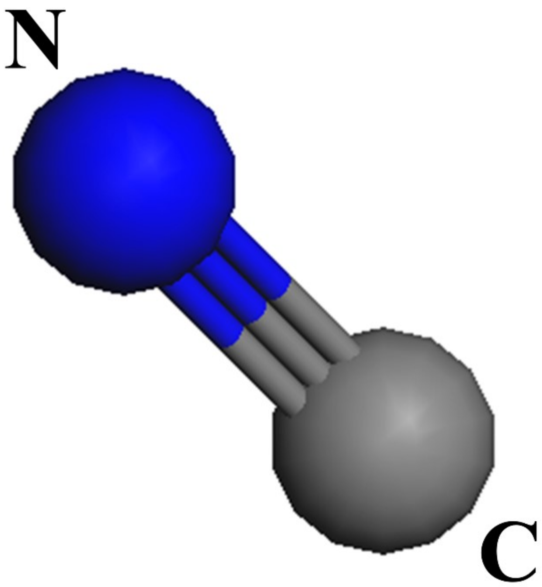

Fig. S2. The structure of CN triple bonds in $FeFe(CN)_6$.

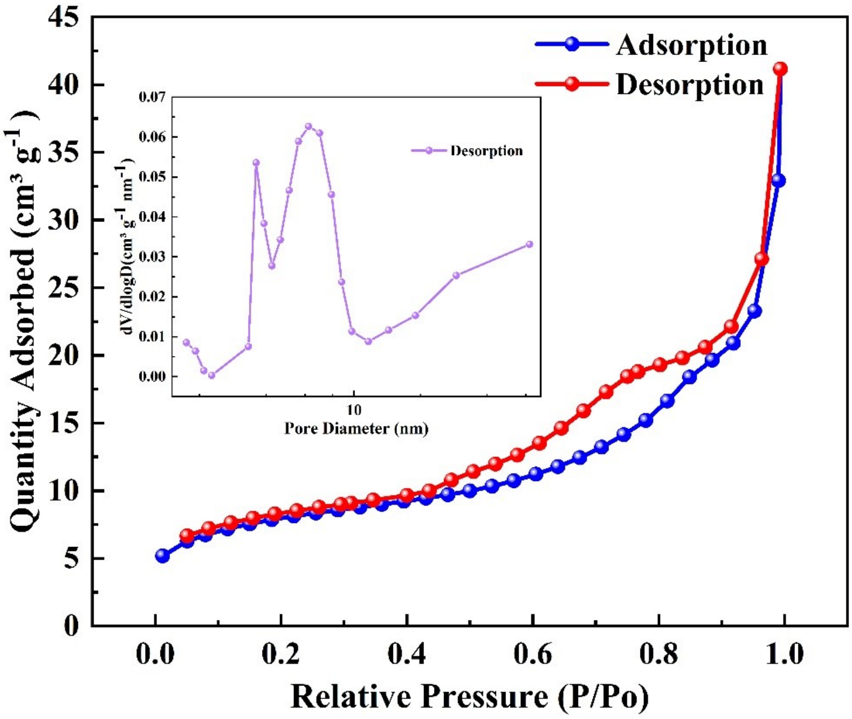

Fig. S3. N_2 adsorption-desorption isotherm and pore-size distribution curve of $FeFe(CN)_6$.

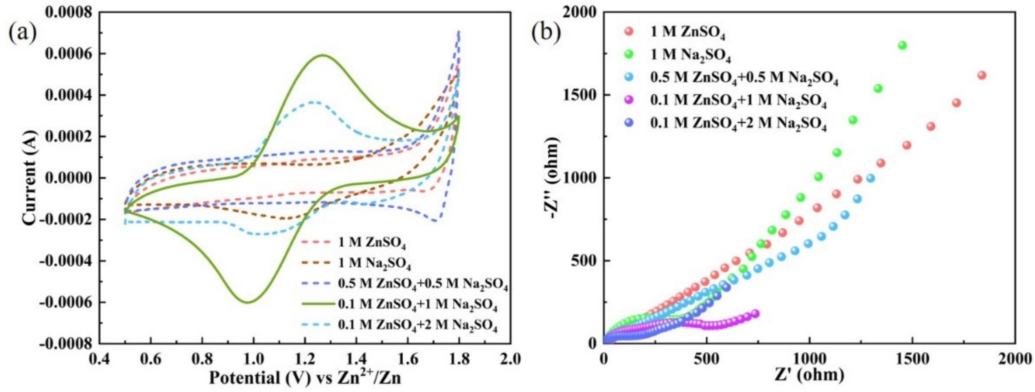

Fig. S4. (a) CV and (b) EIS curves of $FeFe(CN)_6$ after 200 cycles in different electrolytes.

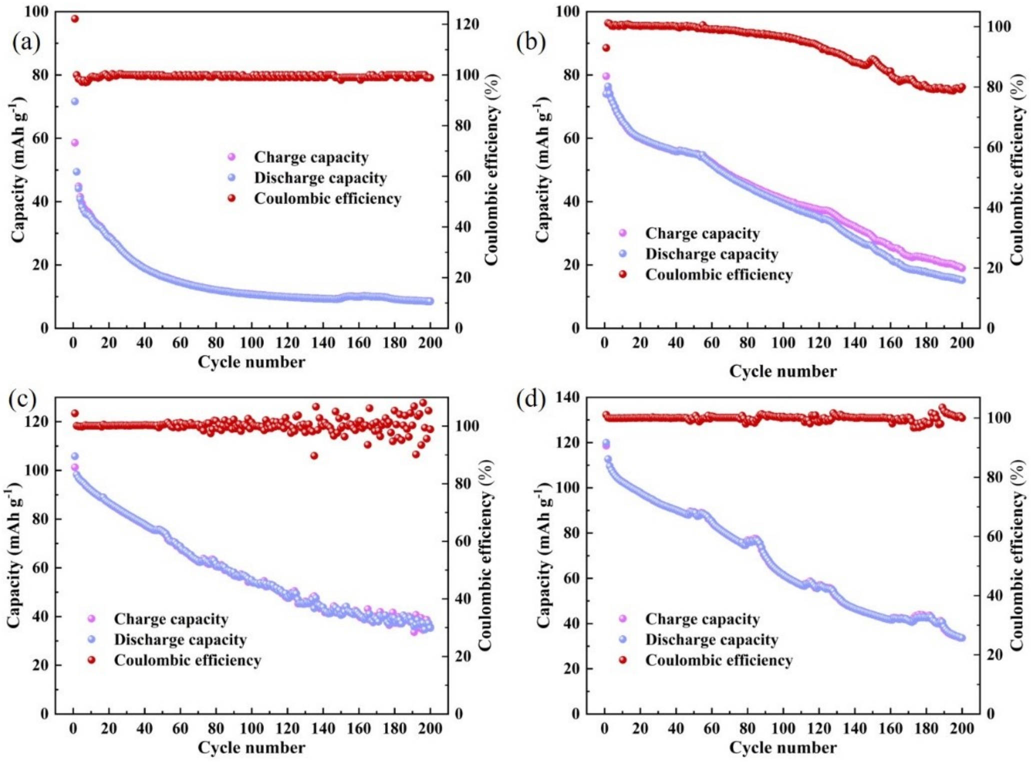

Fig. S5. Cycling performance of Zn//FeFe(CN)$_6$ battery at 1C in different electrolytes: (a) 1 M $ZnSO_4$ electrolyte; (b) 1 M Na_2SO_4 electrolyte; (c) 0.5 M $ZnSO_4$+0.5 M Na_2SO_4 electrolyte; (d) 0.1 M $ZnSO_4$+2 M Na_2SO_4 electrolyte.

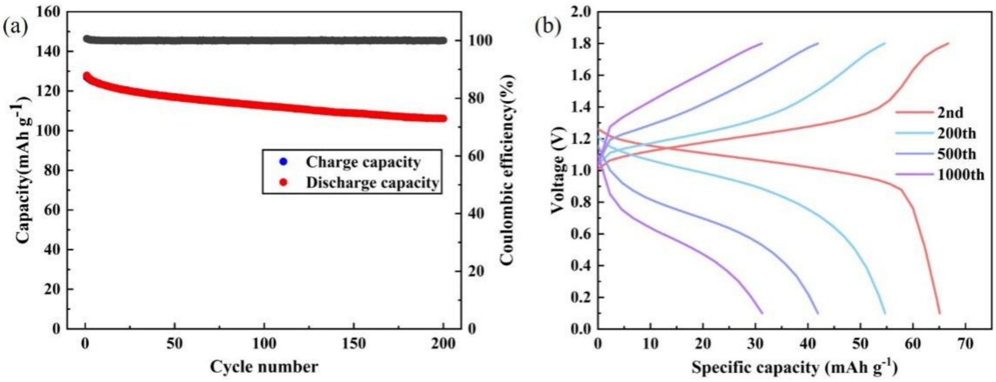

Fig. S6. Electrochemical performances of Zn//FeFe(CN)$_6$ cells in 0.1 M $ZnSO_4$+1 M Na_2SO_4 electrolyte. (a) Cycling performance at 15C for 200 cycles; (b)GCD curves in different cycles at 20C.

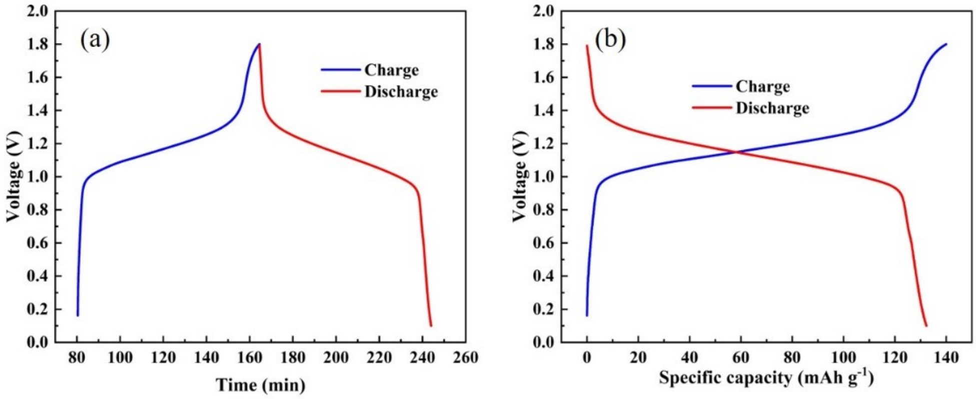

Fig. S7. Charge-discharge curves of Zn//FeFe(CN)$_6$ cells in 0.1 M $ZnSO_4$+1 M Na_2SO_4 electrolyte. (a) The voltage-time and (b) voltage-specific capacity.

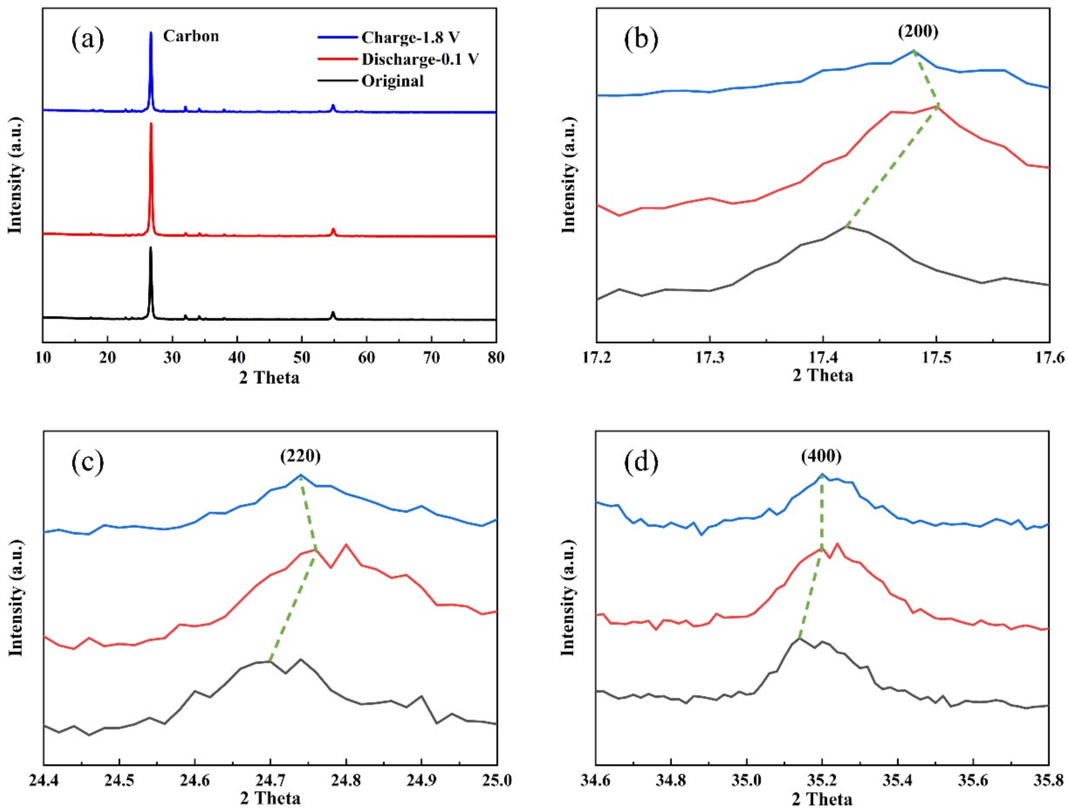

Fig. S8. (a) XRD patterns of the FeFe(CN)$_6$ electrodes under different states after testing in the 0.1 M $ZnSO_4$+1 M Na_2SO_4 electrolyte; (b-d) The magnifications of (200), (220) and (400) peaks.

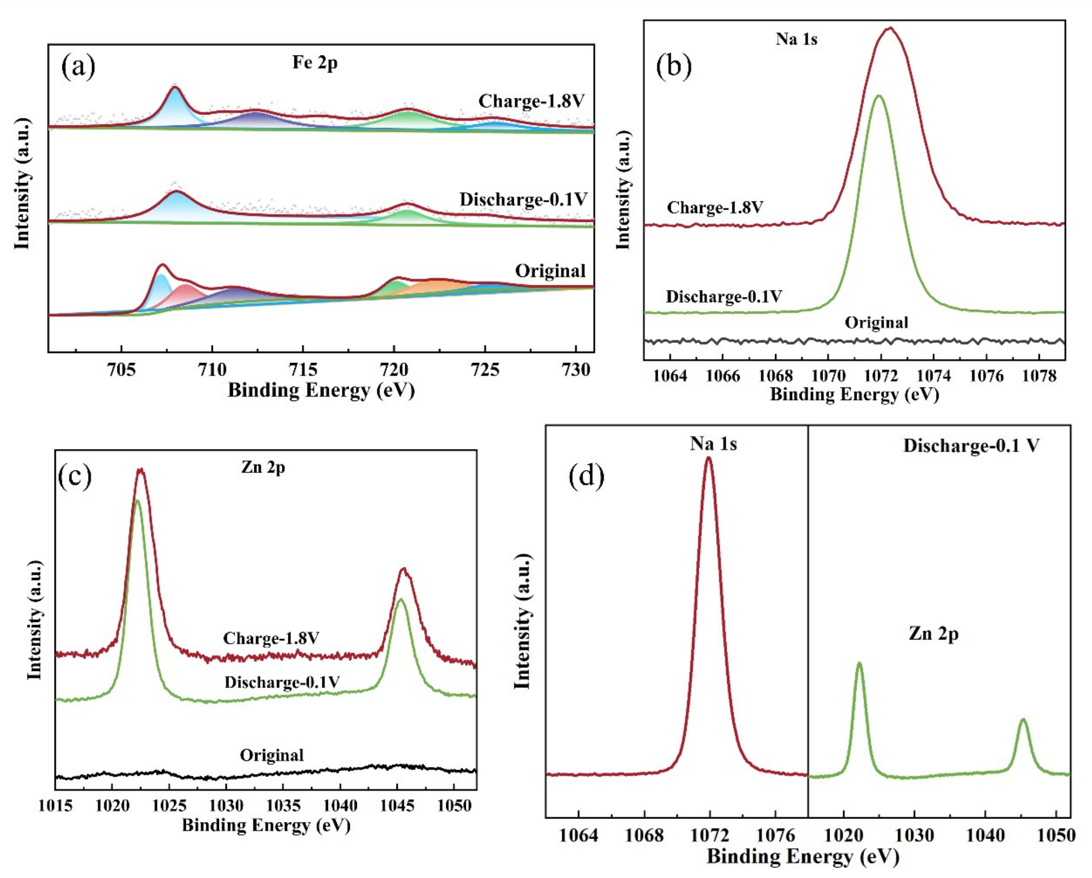

Fig. S9. XPS spectra of high resolution Fe 2p (a), Na 1s (b), and Zn 2p (c) in the $FeFe(CN)_6$ electrodes at different states; (d) Comparison of Na1s and Zn2p when the $FeFe(CN)_6$ electrode is discharged to 0.1V.

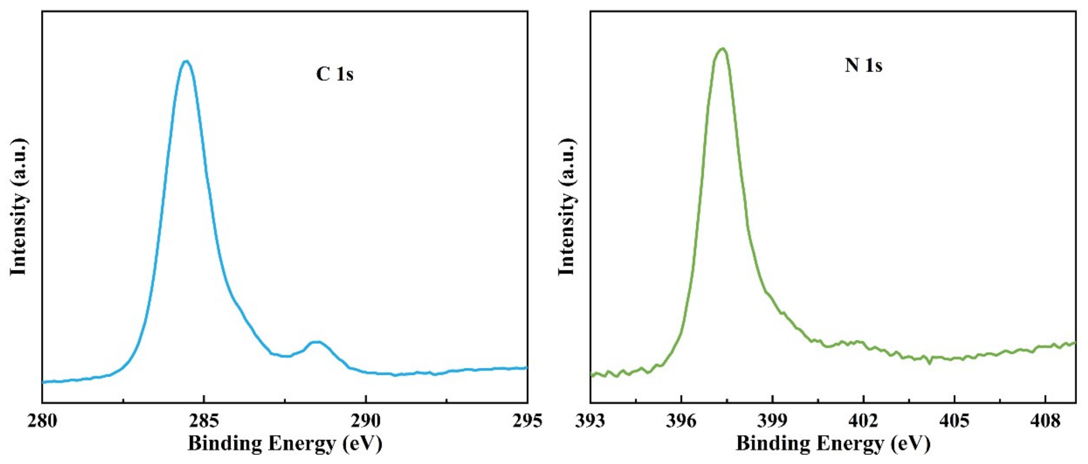

Fig. S10. XPS spectra of high resolution C 1s and N 1s in the $FeFe(CN)_6$ electrodes.

Table S2. Comparison of the electrochemical performances of the Zn//$FeFe(CN)_6$ with other reported Zinc-ion batteries.

Materials	**Electrolyte**	**Specific capacity at *x* A g^{-1}**	**Capacity retention at *y* A g^{-1} after *n* cycles**	**Ref.**
$CuFe(CN)_6$	0.02 M $ZnSO_4$	53 (*x*=0.06)	96% (*n*=100, *y*=60)	1
$Zn_3[Fe(CN)_6]_2$	3 M $ZnSO_4$	66.5 (*x*=0.06)	81% (*n*=200, *y*=0.3)	2
$Zn_3[Fe(CN)_6]_2$	1 M $ZnSO_4$	65.4 (*x*=0.06)	80% (*n*=200, *y*=0.3)	3
$Na_2MnFe(CN)_6$	1 M $ZnSO_4$ with sodium dodecyl sulfate	140 (*x*=0.16)	75% (*n*=2000, *y*=0.8)	4
$CuFe(CN)_6$	1 M Na_2SO_4+0.01 M H_2SO_4	60 (*x*=0.06)	97% (*n*=500, *y*=0.3)	5
$NiFe(CN)_6$	0.5 M Na_2SO_4+50*10^{-3} M $ZnSO_4$	76.2 (*x*=0.1)	81% (*n*=1000, *y*=0.5)	6
$FeFe(CN)_6$	0.1 M $ZnSO_4$+1 M Na_2SO_4	165.2 (0.1C)	84% (*n*=200, *y*=15C)	This work

Table S3: The fitting results of the EIS data according to the equivalent circuit of [R(C[R(Q[RW])])], fitted by Zsimpwin software.

Components	**1 M $ZnSO_4$**	**1 M Na_2SO_4**	**0.5 M $ZnSO_4$+ 0.5 M Na_2SO_4**	**0.1 M $ZnSO_4$+1 M Na_2SO_4**	**0.1 M $ZnSO_4$+2 M Na_2SO_4**
R_s (ohm*g)	3.54*10^{-3}	1.57*10^{-3}	1.90*10^{-3}	5.24*10^{-3}	1.40*10^{-3}
C_f (F)	5.50*10^{-7}	5.54*10^{-6}	4.90*10^{-6}	4.43*10^{-6}	4.44*10^{-6}
R_f (ohm*g)	1.74*10^{-13}	3.47*10^{-9}	4.05*10^{-3}	6.90*10^{-3}	1.18*10^{-2}
Q-Y_o	2.90*10^{-5}	3.92*10^{-4}	1.97*10^{-4}	3.70*10^{-4}	4.15*10^{-4}
Q-n	0.69	0.43	0.61	0.53	0.51
R_{ct} (ohm*g)	180.6	3.79	0.57	0.70	1.72
W	1.76*10^{8}	1.03*10^{-2}	1.53*10^{7}	1.65*10^{-2}	2.67*10^{-3}

Supplementary References:

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