

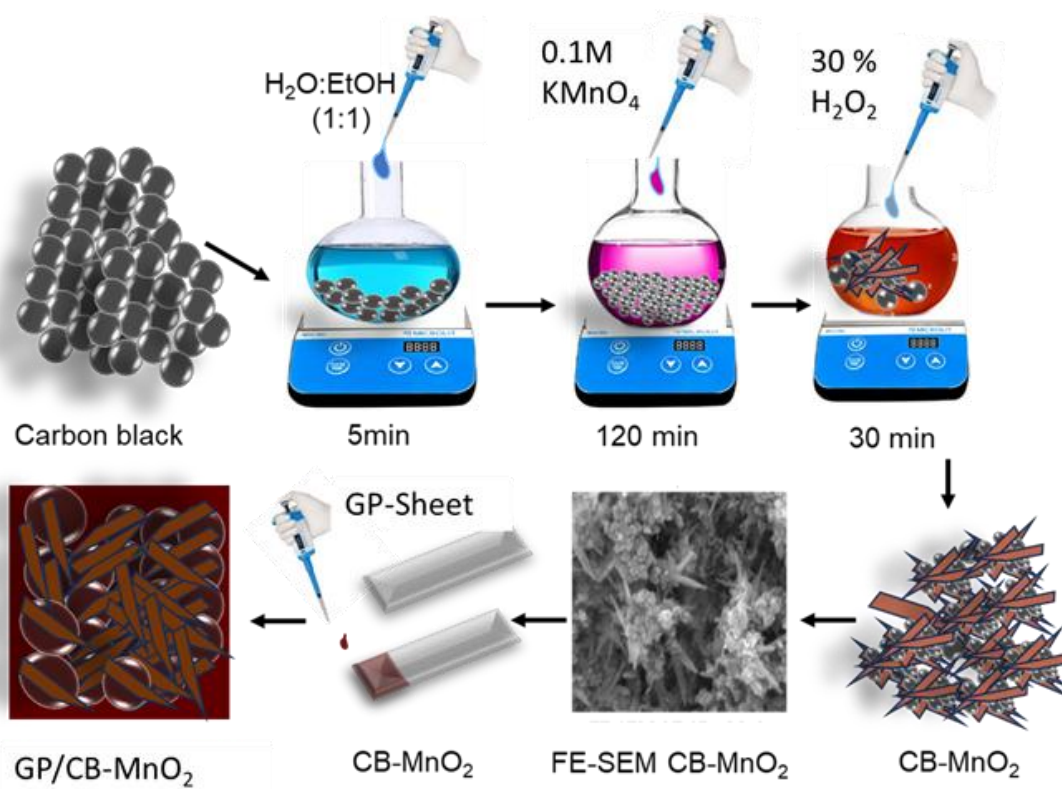
Supporting Information

**A High-Capacity 2.5 V Aqueous K^+/Zn^{2+} Mixed Ions Hybrid
Supercapacitor Enabled by an Electrochemically Pre-Intercalated
 α - MnO_2 /Carbon Black Cathode**

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Supporting Scheme 1. Systematic synthesis procedure of CB- MnO_2

Supporting Table S1. Comparison of Raman shifts various optimal and control materials

System	D band/ cm ⁻¹	G band/ cm ⁻¹	α -MnO ₂ / cm ⁻¹	ZnO/ cm ⁻¹	I _D /I _G
1. CB	1354	1596	-	-	0.63
2. α-MnO₂	-	-	660, 550, 480	-	-
3. CB-MnO₂	1340	1610	570, 644	-	1.19
4. CB-MnO₂@Zn	1349	1591	660	430	1.04

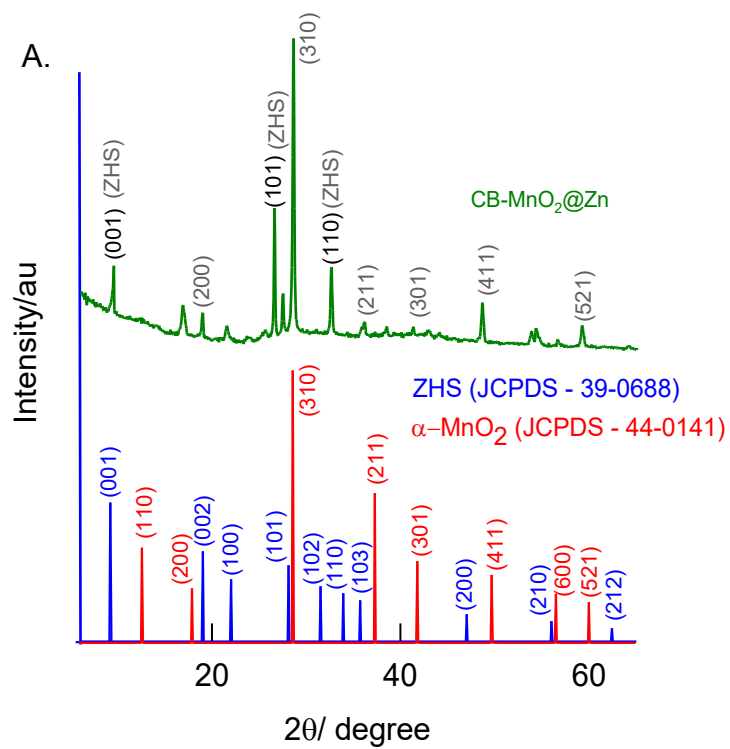
Supporting Table S2. Comparison of various MnO₂ based supercapacitors reported in the literature

S.No	Electrode	Electrolyte	Operation Potential (V)	Capacitance @ Current density	Capacitance retention (Cycles)	Ref
1	CFP- α -MnO ₂	1 M NaSO ₄	0 – 1	472 Fg ⁻¹ @ 1 Ag ⁻¹	92% (10000)	S1
2	α -MnO ₂ @rGO	PVA+CMC+EG	0 – 2	575.5 mFg ⁻¹ @ 6 mA cm ⁻²	89.1% (5000)	S2
3	g-CN/ MnO ₂	2 M KOH	0 – 0.5	148.66 Fg ⁻¹ @ 0.5 Ag ⁻¹	50% (3000)	S3
4	NMOC	1 M NaSO ₄	0 – 1.2	182 Fg ⁻¹ @ 1 Ag ⁻¹		S4
5	α -MnO ₂	1 M NaSO ₄	0 – 1	324 Fg ⁻¹ @ 0.5 Ag ⁻¹	82% (5000)	S5
6	MnO ₂ /rGO	1 M NaSO ₄	-0.1 – 0.9	381 Fg ⁻¹ @ 5 Ag ⁻¹	84% (2000)	S6
7	CD/CNF@MnO ₂	6 M KOH	-0.2 – 0.8	235 Fg ⁻¹ @ 1 mA cm ⁻²	96% (10000)	S7
8	AMCM-4	1 M NaSO ₄	-1 – 0	450 Fg ⁻¹ @ 1 Ag ⁻¹	92.3% (5000)	S8
9	MnO ₂ /MnO@CF	1 M NaSO ₄	0 – 1	216 Fg ⁻¹ @ 1 Ag ⁻¹	100% (10000)	S9
10	MnO ₂ -g-C ₃ N ₄ /C	3 M KOH	0 – 0.6	276 Fg ⁻¹ @ 0.5 Ag ⁻¹	96% (1000)	S10
11	N-PCH@WC-Mn	6 M KOH	0 – 1	434 Fg ⁻¹ @ 1 mA cm ⁻²	96% (10000)	S11
12	G-HMC	6 M KOH	-1 – 0	770.8 Fg ⁻¹ @ 0.5 Ag ⁻¹		S12
13	MnO ₂ /PAC	1 M NaSO ₄	-1 – 0	208.75 Fg ⁻¹ @ 1 Ag ⁻¹	87.43% (5000)	S13
14	ZnMO@CC	1 M NaSO ₄	0 – 1	667 Fg ⁻¹ @ 1 Ag ⁻¹		S14
15	MnO ₂ -BPCs	0.5 M (NH ₄) ₂ SO ₄	-1 – 0	223.2 Fg ⁻¹ @ 0.5 Ag ⁻¹	85% (10000)	S15
16	RAC/MnO ₂	6 M KOH	-1 – 0.2	673 Fg ⁻¹ @ 1 Ag ⁻¹		S16
17	WRC-MnO ₂	1 M NaSO ₄	0 – 0.8	214 Fg ⁻¹ @ 1 mA cm ⁻²	85.27% (5000)	S17
18	δ -MnO ₂ @CC	0.5 M NaSO ₄	0 – 0.9	205 Fg ⁻¹ @ 1 mA cm ⁻²		S18
19	A-MnO ₂ /CC	1 M NaSO ₄	0 – 1	202 Fg ⁻¹ @ 5 mA cm ⁻²		S19
20	MnO ₂ /BC	1 M NaSO ₄	0 – 1	205.5 Fg ⁻¹ @ 0.5 Ag ⁻¹	96.1% (1000)	S20
21	CB-α-MnO₂@Zn	1 mM ZnSO₄ + 0.1 M KCl	0 – 1	811.66 Fg⁻¹ @ 1 Ag⁻¹	80% (5000)	This work

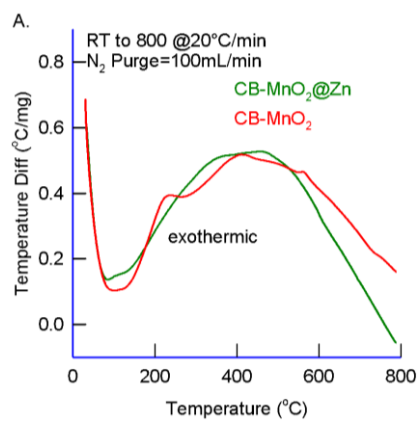
Supporting Table S3. Comparison of various MnO₂ based battery works reported in literature

S.No	Preparation method	Cathode	Electrolyte	Operation Potential (V)	Capacity/ Current density	Energy Density	Power Density	Capacity Retention (cycles)	Ref
1	Hydrothermal & electrochemical	γ -MnO ₂ @CP	2 M ZnSO ₄ + 0.1 M MnSO ₄	0.8 - 1.8	391 mAh g ⁻¹ @ 0.1 Ag ⁻¹	553.12 Wh kg ⁻¹	-	92.17% (3000)	S21
2	Laser modification	Gr- MnO ₂	2 M ZnSO ₄ + 0.1 M MnSO ₄	1 - 2	233 mAh g ⁻¹ @ 1 Ag ⁻¹	-	-	71% (1000)	S22
3	Hydrothermal	C@MnO ₂ -NFs	2 M ZnSO ₄ + 0.1 M MnSO ₄	0.8 - 2	402 mAh g ⁻¹ @ 0.2 Ag ⁻¹	224.2 Wh kg ⁻¹	121 W kg ⁻¹	95% (1000)	S23
4	Hydrothermal	MnO-C@C	2 M ZnSO ₄ + 0.1 M MnSO ₄	0.3 - 1.8	409 mAh g ⁻¹ @ 50 mAg ⁻¹			88% (1000)	S24
5	Hydrothermal	NC@Mn ₃ O ₄	2 M ZnSO ₄ + 0.1 M MnSO ₄	0.8 – 1.8	420 mAh g ⁻¹ @ 1 Ag ⁻¹			90.34% (1000)	S25
6	Hydrothermal	CNT@ β -MnO ₂	2 M ZnSO ₄ + 0.1 M MnSO ₄	0.8 – 1.9	259 mAh g ⁻¹ @ 3 Ag ⁻¹			96% (2000)	S26
7	Hydrothermal	N-doped MnO ₂ -C	2 M ZnSO ₄ + 0.2 M MnSO ₄	0.8 – 1.8	339 mAh g ⁻¹ @ 0.1 Ag ⁻¹			82.8% (1000)	S27
8	Hydrothermal	K-MnO ₂ /CC	2 M ZnSO ₄ + 0.4 M MnSO ₄	1 – 1.8	3.54 mAh cm ⁻² @ 1 mA cm ⁻²	198.6 Wh kg ⁻¹	118.8 kW kg ⁻¹	72.2% (1000)	S28
9	Electrodeposition	PANI-MnO ₂ /CC	2 M ZnSO ₄ + 0.2 M MnSO ₄	0.8 – 1.9	285 mAh g ⁻¹ @ 0.5 Ag ⁻¹	333.3 Wh kg ⁻¹	588.6 W kg ⁻¹	61.7% (800)	S29
10	Hydrothermal	CA@MnO ₂	2 M ZnSO ₄ + 0.2 M MnSO ₄	1 – 1.9	480 mAh g ⁻¹ @ 0.5 Ag ⁻¹	420 Wh kg ⁻¹	6.5 kW kg ⁻¹	88% (1000)	S30
11	Ball milling	β -MnO ₂ /3D GPE-CNT	2 M ZnSO ₄ + 0.5 M MnSO ₄	1 – 1.8	521 mAh g ⁻¹ @ 100 mAg ⁻¹			83% (8000)	S31
12	Hydrothermal	Mn ₂ O ₃ /CDs	3 M ZnSO ₄ + 0.2 M MnSO ₄	0.8 – 1.8	252 mAh g ⁻¹ @ 0.1 Ag ⁻¹			71.6% (1000)	S32
13	Hydrothermal & coprecipitation	MC-MnO ₂	2 M ZnSO ₄ + 0.1 M MnSO ₄	0.6 – 1.9	227 mAh g ⁻¹ @ 0.2 Ag ⁻¹			86% (3000)	S33
14	Hydrothermal & coprecipitation	β -MnO ₂ -MWCNT	3 M ZnSO ₄ + 0.1 M MnSO ₄	0.8 – 1.8	505 mAh g ⁻¹ @ 0.1 Ag ⁻¹			93.5% (1000)	S34

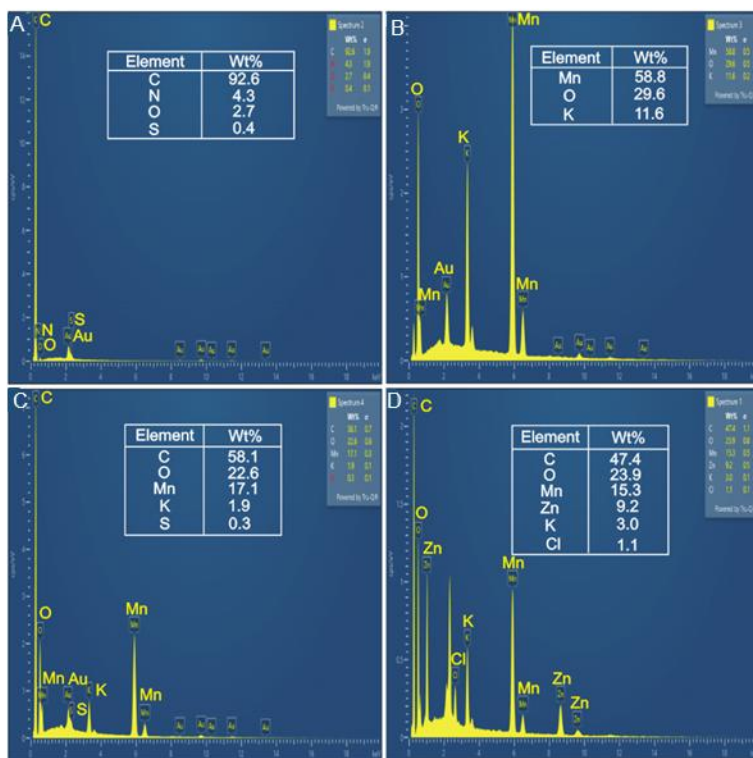
15	Hydrothermal	FMO-CC	0.3 M MnSO ₄ 2 M ZnSO ₄ ⁺ 0.5 M MnSO ₄	0 – 1.8	288 mAh g ⁻¹ @ 1 Ag ⁻¹	47 Wh kg ⁻¹	995 W kg ⁻¹	72% (5000)	S35
16	Hydrothermal & coprecipitation	MnO ₂ /Mn ₂ O ₃ - GO/CNF	6 M KOH	0 – 1.5	222.2 mAh g ⁻¹ @ 1 Ag ⁻¹	24 Wh kg ⁻¹	1554.4 W kg ⁻¹	92% (5000)	S36
17	Simple Co- precipitation method	CB-α- MnO₂@Z n	1 mM ZnSO₄ + 0.1 M KCl	-0.2 – 2.5	315 mAh g⁻¹ @ 0.25 Ag⁻¹	273.4 Wh kg⁻¹	1844.4 W kg⁻¹	94% (5000)	This work



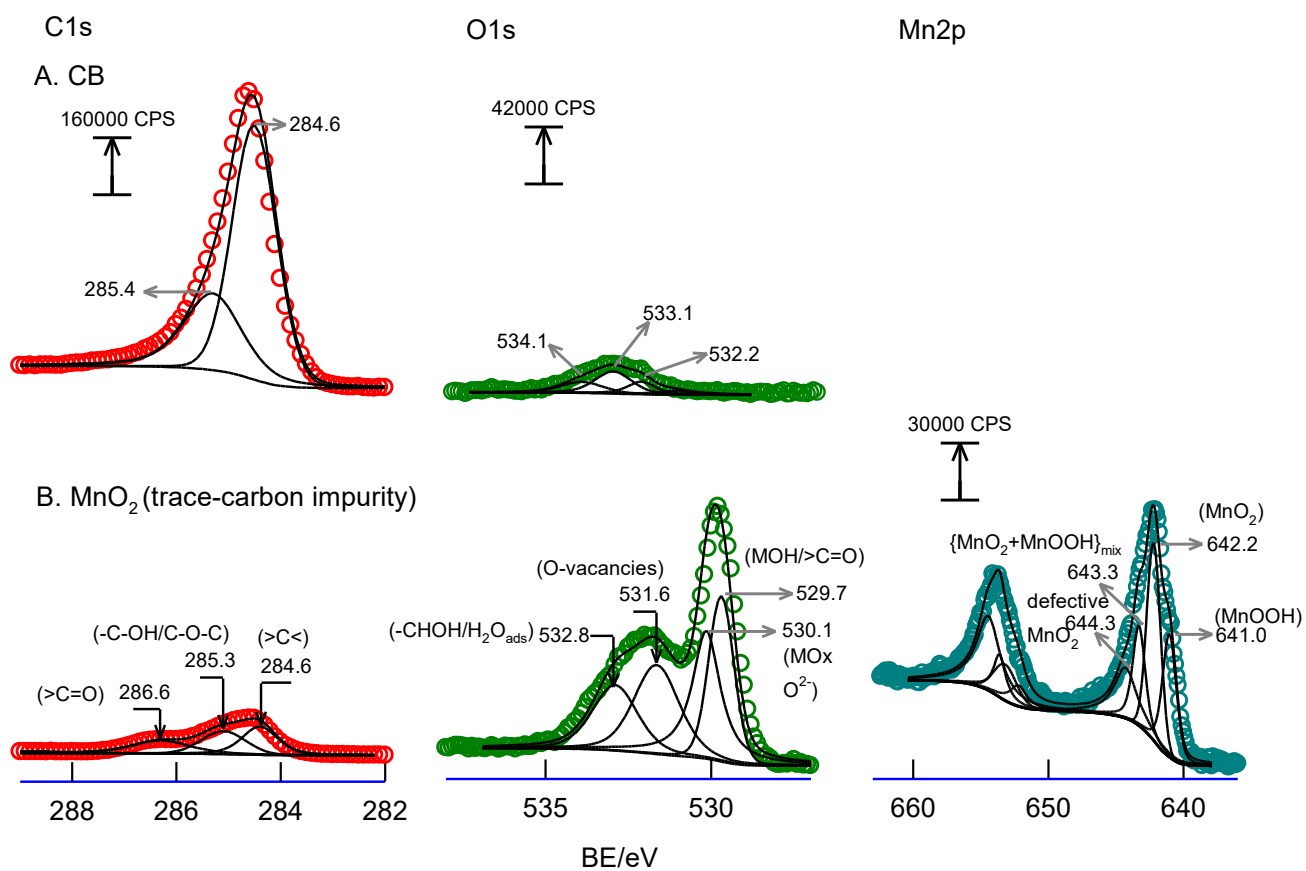
Supporting Figure S1. XRD analysis of CB-MnO₂@Zn and its corresponding JCPDS data.



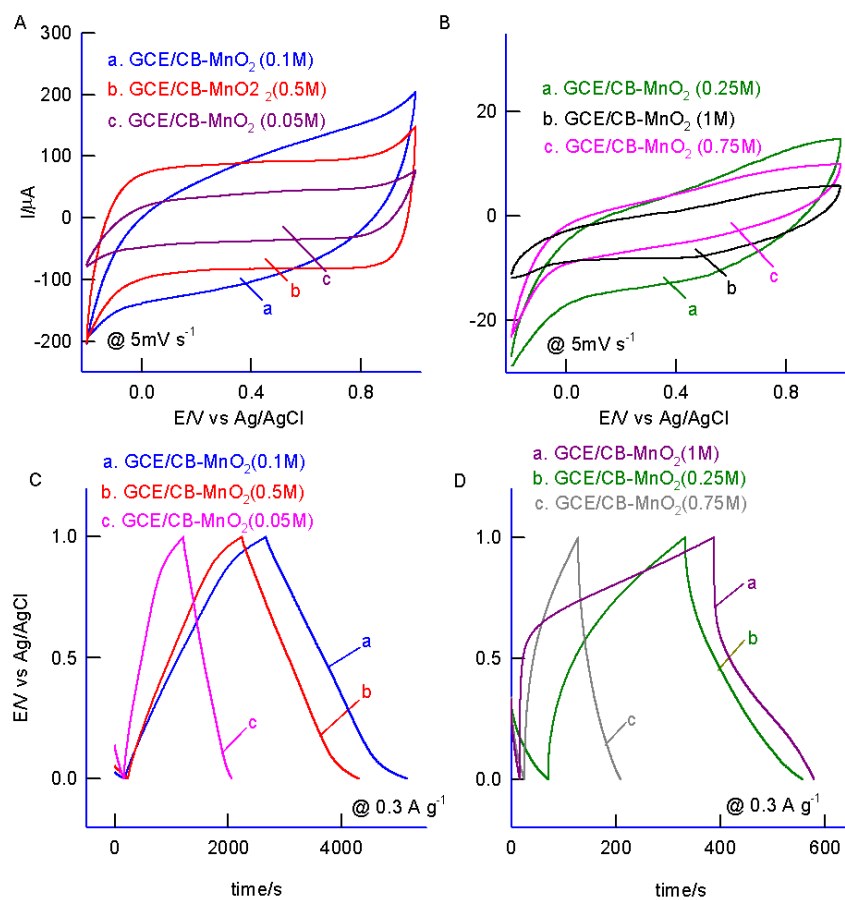
Supporting Figure S2. DTA analysis of CB-MnO₂ and CB-MnO₂@Zn.



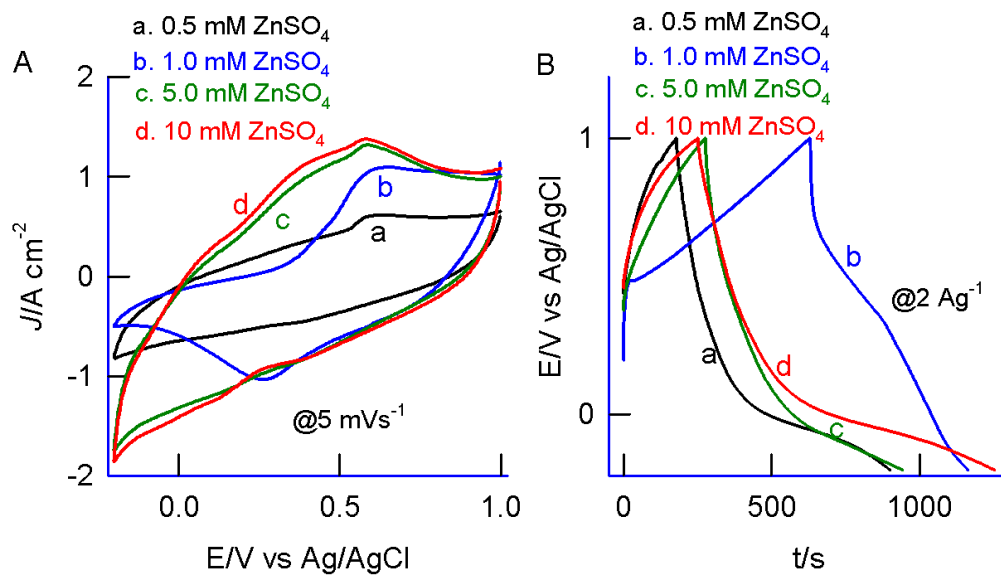
Supporting Figure S3. FESEM EDX analysis of (A) CB, (B) MnO₂, (C) CB-MnO₂ and (D) CB-MnO₂@Zn.



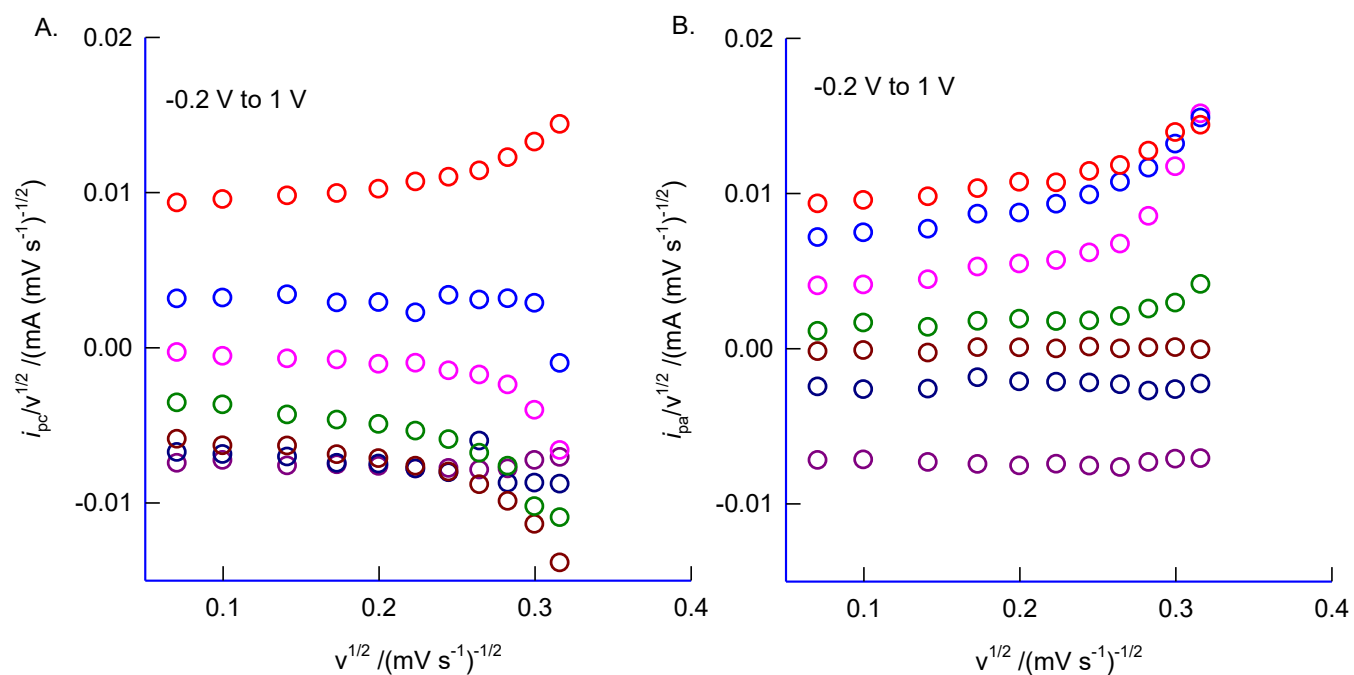
Supporting Figure S4. XPS analysis of (A) CB and (B) MnO₂ for the elements C1s, O1s, Mn2p.



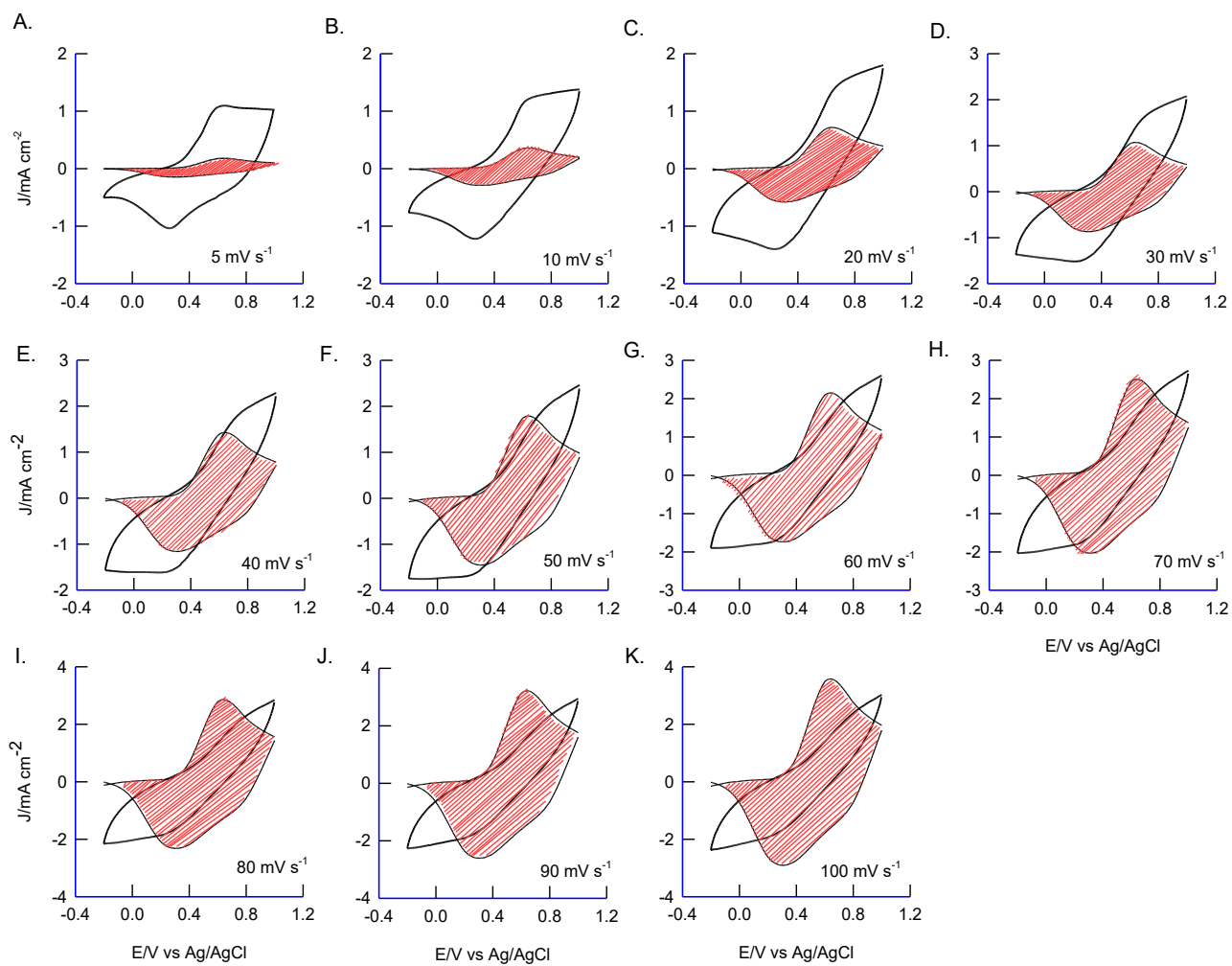
Supporting Figure S5. Cyclic voltammetric (A-B) and GCD (C-D) response of different concentrations of CB-MnO₂, 0.1 M (curve a), 0.5 M (curve b), 0.05 M (curve c) and (B) 0.25 M (curve a), 1 M (curve b) and 0.75 M (curve c).



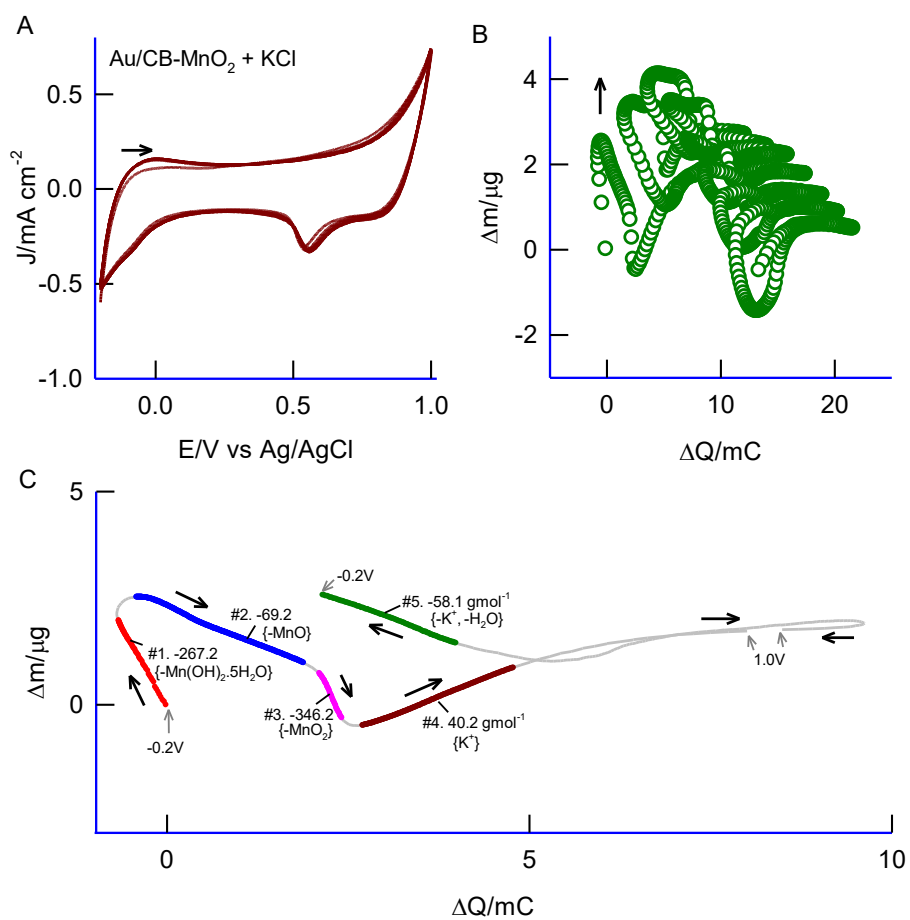
Supporting Figure S6. Optimization of the suitable Zn²⁺ concentration in 0.1 M KCl of CB-MnO₂ cathode using (A) CV, and (B) GCD.



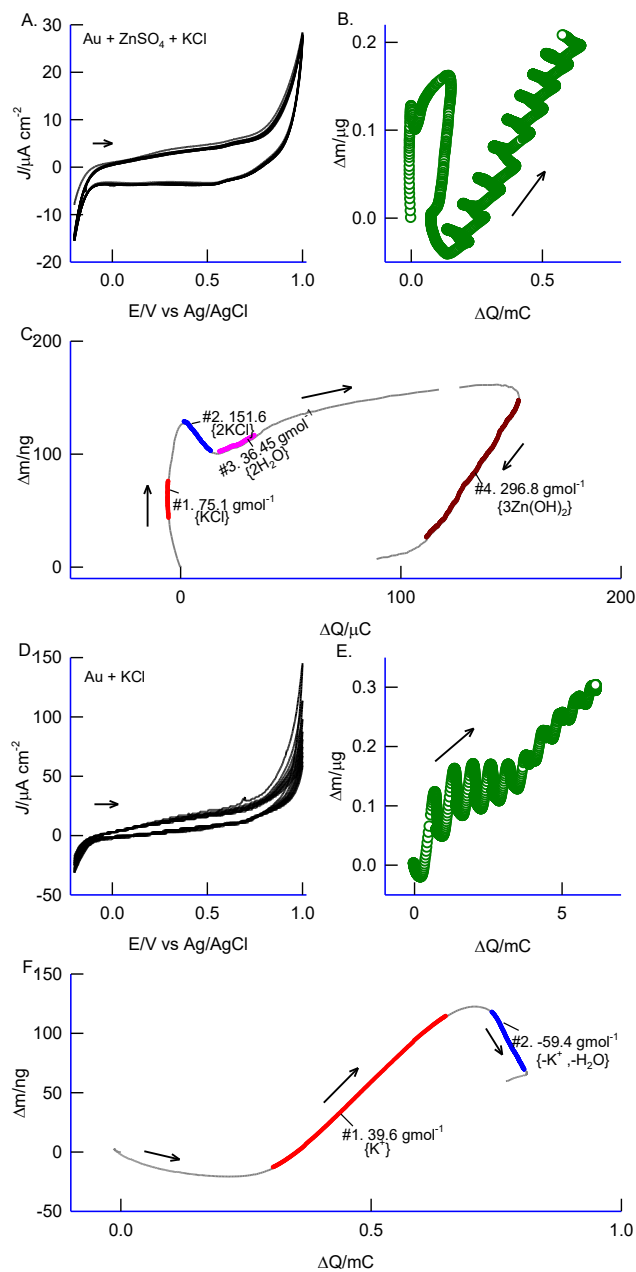
Supporting Figure S7. Analysis of voltammetric sweep data for CB-MnO₂@Zn, sweep rates = 5 mV s⁻¹ to 100 mV s⁻¹.



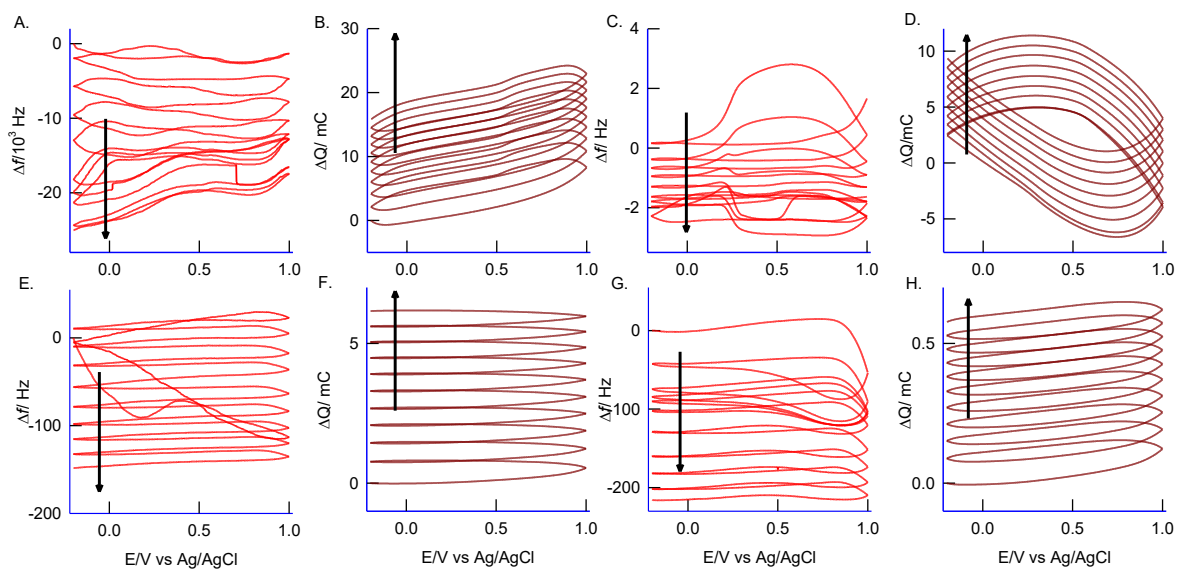
Supporting Figure S8. Dunn's method analysis of capacitive and diffusion contribution of CB-MnO₂@Zn in 0.1 M KCl + 1 mM ZnSO₄ (shaded region = pseudocapacitive contribution).



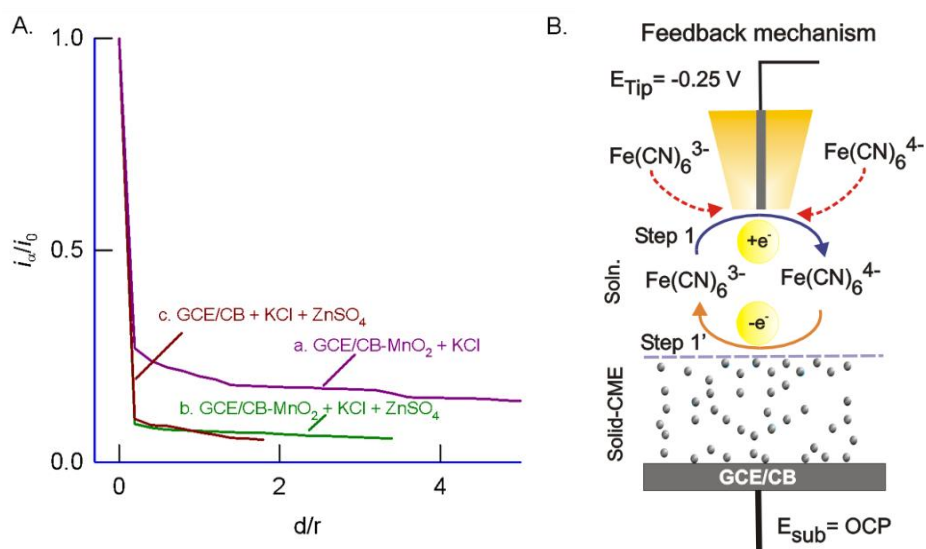
Supporting Figure S9. EQCM responses of Au/CB-MnO₂ (A-C) 0.1M KCl.



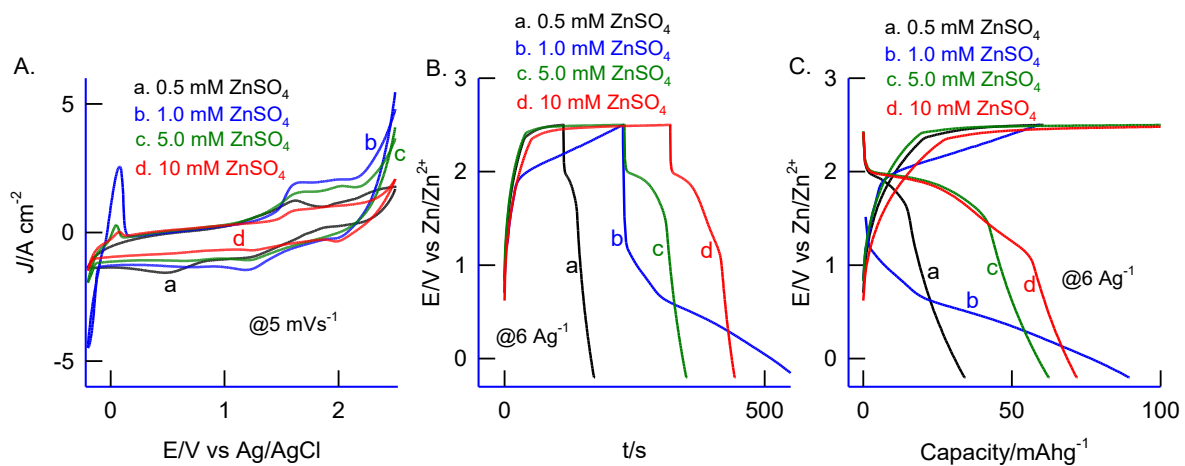
Supporting Figure S10. EQCM responses of EQCM-Au electrode with (A-C) without (D-F) ZnSO_4 containing 0.1M KCl



Supporting Figure S11. EQCM responses of Potential vs frequency and charge. Au/CB-MnO₂ electrode in with (A-B) and without (C-D) ZnSO₄ containing 0.1M KCl. EQCM-Au electrode with (E-F), ZnSO₄ and without (G-H) in KCl.



Supporting Figure S12. (A) SECM approach curves of different electrodes in with and without Zn^{2+} containing KCl. **(B)** Systematic representation of (feedback mode mechanism) GCE/CB in KCl + ZnSO_4 .



Supporting Figure S13. Regulating the Zn²⁺ concentration in (A) CV and (B&C) GCD experiments

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