

Electronic Supplementary Information

Transition Metal Phosphide-based Oxygen Electrocatalysts for Aqueous Zinc-Air Batteries

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Table S1. List of TMPs synthesizes using electrochemical technique.

| Catalyst | Deposition technique & deposition time | Potential/ Current/ Frequency | P source | Additive | Current collector | Ref. |
|--------------------|--|---|---|---|---------------------|------|
| Ni-Co-Mn phosphide | 3E ^a Galvanostatic 2.5 h | -10 mA cm ⁻² | NaH ₂ PO ₂ · H ₂ O | Pluronic P123, NH ₄ Cl | Ni foam | 1 |
| NiCoP/CC | 2E DC voltage 60 min | -2.0 V | NaH ₂ PO ₂ · 6H ₂ O | - | Carbon cloth | 2 |
| Ni-Fe-P | 3E ^b Pulse 600-2400 s | -0.3 to -1.2 V; 0.01, 0.1, 1 Hz | NaH ₂ PO ₂ · H ₂ O | Trisodium citrate dehydrate | Copper substrate | 3 |
| NiFeP/NM | 2E Monopulse 0-2400 s | 50 and 250 mA cm ⁻² ; 50 Hz, 35 Hz, 0.5 Hz, 0.05 Hz | NaH ₂ PO ₂ · H ₂ O | NH ₄ Cl | Ni mesh | 4 |
| Ni-Cu-P@Ni-Cu | 2E and 3E ^b Galvanostatic and CV 4.8 min | 2 A cm ⁻² ; -0.4 to -1.4 V@20 mV s ⁻¹ for 10-50 cycles | NaH ₂ PO ₂ · H ₂ O | Trisodium citrate dehydrate | Ni foam | 5 |
| FeMnS/FeMnP/NF | 3E ^a CV | -1.2 to 0.2 V @5 mV s ⁻¹ for 20 and 30 cycles | NaH ₂ PO ₂ · H ₂ O | - | Ni foam | 6 |
| FeP | 3E ^b Potentiostatic 360 s | -1.7 V for 120 s, then immediately switched into -0.1 V for 240 s (Repeat 7 times) | NaH ₂ PO ₂ | Formic acid (1 vol.%) | Cu Foil | 7 |
| Ni-P | 3E ^a Galvanostatic 15 min | -250 mA | NaH ₂ PO ₂ · H ₂ O | - | Ni Foam | 8 |

| | | | | | | |
|---|--|---|---|--|---------------------------------|----|
| Ni-Co-P | 3E ^b CV 10 cycles | -0.2 to -1.3 V@20 mV/s | NaH ₂ PO ₂ · H ₂ O | Trisodium citrate dehydrate | Ni nanosheets/ Ni Foam | 9 |
| Co-P | 3E Galvanostatic 60 s | 2.0 A·cm ⁻² | NaH ₂ PO ₂ | C ₇ H ₅ NO ₃ S | Ni Foam | 10 |
| Cu-Co-P _x | 2E DHBT (Galvanostatic) 20 s | 2.0 A·cm ⁻² | NaH ₂ PO ₂ | - | Stainless steel foil | 11 |
| Ni-Mo-P | 3E ^b Galvanostatic 60 min | -60 mA cm ⁻² | NaH ₂ PO ₂ · H ₂ O, | C ₆ H ₅ Na ₃ O 7·2H ₂ O | Ni Foam | 12 |
| Co ₂ P | 3E ^b Potentiostatic 10 min | -1.0 V | NaH ₂ PO ₂ · H ₂ O | - | Ni Foam | 13 |
| NiP | 3E ^a Potentiostatic 300 s | -1.0 V | NaPO ₂ H ₂ | 3-MPA | Ni Foam | 14 |
| Ni-Co-P | 3E ^b Galvanostatic | 350 mA cm ⁻² | H ₃ PO ₃ , H ₃ PO ₄ | - | Circular copper foil | 15 |
| NiMoP/CuF | 2E and 3E ^a Galvanostatic 2 min, 5 min | 160 mA cm ⁻² , 100– 180 mA cm ⁻² | Na ₂ H ₂ PO ₄ ·H ₂ O | Sodium citrate tribasic dihydrate | Copper foam | 16 |
| Co– P/Fe ₃ O ₄ @NF | 3E ^a Galvanostatic 25 min | -8 mA cm ⁻² | NaH ₂ PO ₂ · H ₂ O | - | Ni foam | 17 |
| g-C ₃ N ₄ /NiCoP/ NF | 3E ^c Potentiostatic 50-400 s | -1.0 V | NaH ₂ PO ₂ | NH ₄ Cl | Ni foam | 18 |

| | | | | | | |
|----------------------|---|-------------------|---|---|---------|----|
| Ni ₃ P/NF | 3E ^a Potentiostatic 5400 s | -0.8 V and -1.1 V | NaH ₂ PO ₂ · H ₂ O, NaH ₂ PO ₄ | - | Ni foam | 19 |
|----------------------|---|-------------------|---|---|---------|----|

3E = Three-electrode set-up

2E = Two-electrode set-up

a = Ag/AgCl; b = SCE; c = Hg/HgO

Table S2. List of monometallic TMPs for bifunctional electrocatalysis and ZAB performance.

| Catalyst | ΔE (V) | ^a OCV (V) | Specific capacity (mA h g ⁻¹) | ^b PPD (mW cm ⁻²) | Energy density (mWh g ⁻¹ _{zn}) | Cyclic stability (h) | Ref. |
|---|-------------------|-------------------------|---|--|---|--------------------------------|-------------|
| CoP@PNC | 0.78 | - | 730.5 ^f | 138.57 | - | 150 ⁱ | 20 |
| Co ₂ P@NPPC | 0.70 | 1.4 | 797 ^f | 226 | - | 160 ^f | 21 |
| CoP@C/CNSs | 0.79 | 1.49 | 750.8 ^f | 180.1 | 916 | 80 ^f | 22 |
| Co ₂ P@NCNTs | 0.93 | 1.3 | 792.6 ^f | 159.7 | 921.2 | 100 ^f | 23 |
| Co ₂ P@NCNT-4 | 0.87 | - | 831.25 ^f | 217 | - | 240 ^f | 24 |
| H-CoP@NC | - | 1.51 | - | 152.94 | - | 123 ^j | 25 |
| Co ₂ P@NPCNTs | - | 1.43 | - | 65.83 | - | 30 ^f | 26 |
| CoP@NWC | 0.65 | 1.50 | 805.8 ^f | 175 | - | 407 ^f | 27 |
| Co _x P@NPC | 0.75 | 1.43 | - | 157 | - | 140 ^f | 28 |
| CoP@CF-900 | - | 1.40 | 776 ^f | 150 | - | 150 ^f | 29 |
| Co ₂ P@CNF | - | 1.393 | - | 121 | - | 23 ^f | 30 |
| Co ₂ P/NPG | 0.82 | 1.42 | - | 103.5 | - | 55 ^c | 31 |
| CoP/NP-HPC | - | 1.4 | - | 186 | - | 80 ^c | 32 |
| Co ₂ P@NC | 0.65 | 1.44 | - | 81.3 | - | 283 ^f | 33 |
| FeP@NPW | 0.65 | 1.53 | 811.7 ^e | 162 | - | 339 ^e | 34 |
| FeP@NPC-900 | 0.67 | 1.46 | 785 ^j | 190.15 | 706.5 | 35 ^e | 35 |
| FeP _{0.6} @CNP100 0 | - | 1.455 | - | 80 | - | 58 ^f | 36 |
| Fe ₂ P/NPC | - | 1.4697 | 654.1 ^f | 111.16 | 733.6 | - | 37 |
| FeP-NWCC | 0.68 | 1.50 | 805.6 ^f | 144 | - | 450 ^f | 38 |
| Fe-N ₄ -Fe ₂ P NPs/NPC | - | 1.57 | 729.5 ^f | 140.3 | 817.9 | 300 ^e | 39 |
| Fe ₂ P/NPCt | - | 1.402 | 744.1 ^f | 175.48 | 884.8 | - | 40 |

| | | | | | | | |
|---|-----|-------|---------------------|--------|-----|------------------|----|
| CV- FeP/NPCNT-30 | - | 1.528 | 851.5 ^e | 221 | - | 78 ^e | 41 |
| Vp-Ni ₂ P@NC | 0.7 | 1.46 | - | 203.48 | - | 150 ^f | 42 |
| Ni ₂ P@NPC | 0.8 | 1.46 | 770.25 ^f | 162 | 692 | 100 ^e | 43 |
| Ni _x P-NP-C | - | - | - | 266 | - | 30 ^e | 44 |
| NPO/Ni _x P _y @NF -HPCs | - | 1.441 | - | 337 | - | 15 ^c | 45 |

Table S3. List of multimetallic TMPs for bifunctional electrocatalysis and ZAB performance.

| Catalyst | ΔE (V) | ^a OCV (V) | Specific capacity (mA h g ⁻¹) | ^b PPD (mW cm ⁻²) | Energy density (mWh g ⁻¹ _{zn}) | Cyclic stability | Ref. |
|---|-------------------|-------------------------|---|--|---|---|------|
| FeCoP@NC | 0.86 | 1.56 | 793.6 ^f | 183.5 | - | 150 ^d | 46 |
| FeCoP ₂ -CNc | 0.81 | 1.41 | 764.6 ^d | 122.5 | - | 45 ^d | 47 |
| MoCoP-NPC | 0.66 | 1.50 | 829.6 ^g | 175.2 | 994.8 | 300 ^f | 48 |
| FeCoP/NPC | 0.75 | 1.51 | 807 ^e | 136 | - | 950 ^f | 49 |
| CoFeP@C | 0.86 | - | 783.6 ^f | 143.5 | - | 200 ^c | 50 |
| CoP-NC@NFP | 0.83 | 1.44 | - | 93 | - | 200 ^c | 51 |
| Co ₂ P-Fe ₂ P | 0.70 | 1.45 | 728.8 ^f | 152 | | 47 ^f | 52 |
| CoP/Ni ₂ P | | 1.4 | | 77 | | 33.3 | 53 |
| FeNiP@C-200 | 0.70 | - | 786.2 ^f | 169 | - | 220 ^d | 54 |
| FeNiP/NPCS | 0.80 | 1.51 | 602.7 ^f | 163 | 783.5 | 110 ^f | 55 |
| Cr-doped Ni ₂ P@NF | - | 1.42 | 767.8 ^e | 139 | 944.39 | 208 ^e | 56 |
| Cu-Co ₂ P/CNFs | | 1.36 | | 230 | | 80 h ^c | 57 |
| W-Co ₂ P/NC | 0.72 | 1.50 | 881 ^f | 224.4 | 884 | 130 ^f | 58 |
| Cu-Co ₂ P@2D- NPC | | 1.40 | 736.8 ^f | 236.1 | 950 | 160 | 59 |
| | | | | | | (charge 2 mA cm ⁻²) and Discharge 10 mA cm ⁻²) | |
| Mn(0.1)- Co ₂ P/NC | | 1.35 | | 40.44 | | 100 cycles ^g | 60 |
| Fe _{0.20} Co _{0.80} P /PNC | 0.71 | | | 167 | | 92 ^c | 61 |

Table S4. List of heterostructure TMPs for bifunctional electrocatalysis and ZAB performance.

| Catalyst | ΔE (V) | ^a OCV (V) | Specific capacity (mA h g ⁻¹) | ^b PPD (mW cm ⁻²) | Energy density (mWh g ⁻¹ _{zn}) | Cyclic stability | Ref. |
|--|-------------------|-------------------------|---|--|---|--|------|
| CoP/FeP@PCN | 0.56 | 1.52 | 780 ^f | 175.4 | | 579 ^e | 62 |
| CoP@Co ₂ P/NP | 0.78 | 1.56 | 689 ^e | 215.1 | | 580 ^e | 63 |
| C | | | | | | | |
| Fe-P/Cu ₃ P-NPC | 0.74 | 1.39 | 815.3 ^f | 158.5 | | 366 ^b | 64 |
| FeP/Fe ₂ P-NSPC | | 1.41 | 702 ^f | 91 | 737 | | 65 |
| CoP/Co ₂ P/Co ₃ O ₄ | | 1.43 | 710 ^f | 64.4 | | 33.3 ^f | 66 |
| Cu ₃ P/CoP@NC | | 1.42 | 765.6 ^f | 209 | | 317 ^e | 67 |
| Cu ₃ P/MoP@C | - | 1.51 | 704 ^f | 156 | - | 231 ^e | 68 |
| CoP/Co ₂ P@CN | 0.68 | 1.38 | 740.5 ^f | 221 | | 900 ^e | 69 |
| S | | | | | | | |
| CoP ₃ /CeO ₂ /C | | 1.343 | 767.7 ^e | 150 | 871.3 | 120 ^e | 70 |
| Co ₃ O ₄ @Ni ₂ P | | 1.35 | | 182.8 | | 177 ^f | 71 |
| CoP ₃ /CoSnO ₂ | | 1.36 | | 135 | | 120 ^e | 72 |
| Cu ₃ P/TiO ₂ @NC | | 1.30 | 747.3 ^f | 182.9 | | 220 ^e (using RuO ₂) | 73 |
| CoP/CoO@MN C-CNT | | 1.40 | 724.6 ^f | 152.8 | | 500h ^f | 74 |
| NiCoP/NiO | - | 1.43 | 704.9 ^f | 74.74 | - | 182 ^e | 75 |
| NiCoP@CoNi- LDH/SSM | 0.57 | 1.25 | 678.7 ^f | 53.4 | | 1505 ^e | 76 |
| NiCoP/NiFe LDH@CC | - | 1.43 | - | 184 | - | 238 ^f | 77 |
| FeCo- NC@Co ₂ P-NC | 0.674 | 1.47 | 881.3 ^f | 159.3 | | 280 cycles | 78 |

| | | | | | | | |
|--|-------|-------|--------------------|--------|-------|-------------------|----|
| CoNiP/PNC | 0.86 | 1.44 | 729.3 ^f | 171 | | 57 ^f | 79 |
| FeCo-rich phosphides@N, P-doped carbon | 0.73 | 1.57 | | 174 | | 720 ^f | 80 |
| H-CNP@M | 0.691 | 1.44 | 801 ^f | 166.5 | | 120 ^f | 81 |
| Co ₂ P/Co ₃ Fe ₇ @N-C | 0.66 | 1.48 | 858 ^f | 151.6 | | 266 ^c | 82 |
| Fe ₂ P/Co@NPC | 0.685 | | | 233.56 | | 180 ^e | 83 |
| Co/Co ₂ P@NPC NTs | 0.66 | 1.465 | | 189.7 | | 200 ^f | 84 |
| Co/Co ₂ P@NCN T | 0.68 | 1.45 | | 330 | | 1080 ^e | 85 |
| Co ₂ P/Co-NC | 0.72 | 1.45 | 837 ^f | 187 | | 140 ^e | 86 |
| Ni/Ni ₁₂ P ₅ @CN _x | 0.66 | 1.41 | 710 ^h | 181 | | 1000 cycles | 87 |
| Co ₂ P/Co@N-CNT/NPG | 0.82 | 1.45 | 781 ^f | 145 | 987.2 | 800 ^f | 88 |
| Cu/Cu ₃ P@NP-C-900 | | 1.42 | 795.5 ^e | 148.2 | 936.8 | | 89 |
| Co ₂ P/Co-N-C | | 1.5 | 803 ^f | 158 | | | 90 |

^a open circuit voltage; ^b peak power density; ^c at 2 mA cm⁻²; ^d at 3 mA cm⁻²; ^e at 5 mA cm⁻²
^f at 10 mA cm⁻²; ^g at 20 mA cm⁻²; ^h at 25 mA cm⁻²; ⁱ at 30 mA cm⁻²; ^j at 50 mA cm⁻²

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