Supporting Information

A Modified Molecular Framework Derived Highly Efficient Mn-Co-Carbon Cathode for Flexible Zn-air Battery

Hui Cheng,^a Jun-Min Chen,^a Qi-Jia Li,^{b,c} Chang-Yuan Su,^a An-Na Chen,^a Jia-Xuan Zhang,^a Zhao-Qing Liu^{*, a}, Yexiang Tong^c

^aSchool of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou Higher Education Mega Center, Waihuan Xi Road No. 230, Guangzhou, 510006, P. R. China. ^bThe Affiliated High School of South China Normal University, Guangzhou, 510631, P.

R. China.

^cSchool of Chemistry, Sun Yat-Sen University, 135 Xingang West Road, Guangzhou, 510275, P. R. China.

<u>1. Experimental Section</u>

1.1 Materials Characterization

All reagents and chemicals were used without further purification. The carbon nanotubes (CNTs, 99% AR) is obtained from Shenzhen Nanotech Port Co. Ltd. Co(OAc)₂·4H₂O (99% AR), Mn(OAc)₂·4H₂O (99% AR) are purchased from Guangzhou Chemical Reagent Factory. NH₃·H₂O (25-28 wt.%) is purchased from Tianjin Fuyu Fine Chemical Co. Ltd. 20 wt.% Pt/C is purchased from Shanghai Hansi Chemical Industry Co., Ltd. Polyvinylpyrrolidone (PVP, 99% AR) is obtained from Shanghai Tianlian Fine Chemical Co. Ltd.

1.2 Synthesis of catalysts

1.2.1 Oxidization of carbon nanotubes. Carbon nanotubes (CNTs) is firstly modified by the acid treatment. Briefly, 1 g CNTs is added to concentrated sulfuric acid (23 mL) following by adding 1 g of KMnO₄ and 0.4 g of KNO₃. After maintaining at 40 °C for 30 min, 200 mL of double-distilled water and 10 mL of H_2O_2 (30 %) are orderly added to the flask to terminate the oxidization reaction. The oxidized CNTs is washed with double-distilled water and finally lyophilized.

1.2.2 Preparation of $CoMn_2O_4/N$ -CNTs, $MnCo_2O_4/N$ -CNTs, Mn_3O_4/N -CNTs and Co_3O_4/N -CNTs. Briefly, a predetermined amount of $Co(OAc)_2$ ·4H₂O (0.64 mmol) and $Mn(OAc)_2$ ·4H₂O (1.28 mmol) are dispersed in ethanol-water (96 mL of ethanol and 4 mL of double-distilled water) with 0.068 g acid-treated CNTs. 0.5 mL of NH₃·H₂O is added into the mixture after a completely ultrasonic dispersion. The mixture is

stirred at 80 °C for 24 h. The solution thus obtained is then loaded in 50 mL Teflon-lined stainless steel autoclave and kept at 150 °C for 1 h hydrothermal reaction. The precipitate is separated by vacuum filtration and washed by ethanol and water for several times. The fine black powder is obtained after drying the precipitate under vacuum at 80 °C. For a control experiment, $MnCo_2O_4/N-CNT$, $Mn_3O_4/N-CNTs$ and $Co_3O_4/N-CNTs$ are prepared following the same steps as those used for the preparation of $CoMn_2O_4/N-CNT$ with different ratio of metal salt: 1.28 mmol $Co(OAc)_2\cdot4H_2O$ and 0.64 mmol $Mn(OAc)_2\cdot4H_2O$ for $MnCo_2O_4/N-CNT$, 1.93 mmol $Co(OAc)_2\cdot4H_2O$ for $Co_3O_4/N-CNTs$ and 1.93 mmol $Mn(OAc)_2\cdot4H_2O$ for $Mn_3O_4/N-CNTs$.

1.3 Physicochemical Characterizations

Morphology measurements are performed on a field emission scanning electron microscopy (SEM, JEOL-6700F). Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HRTEM) measurements are taken with transmission electron microscopy (TEM, 300 kV, Tecnai[™] G2 F30) operated at 200 kV accelerating voltage. X-ray diffraction (XRD) patterns are obtained by X-ray diffraction measurement on a MiniFlex II diffractometer. X-ray photoemission spectroscopy (XPS) analyses were performed on is carried out by X-ray Photoelectron Spectroscopy (XPS, ESCALAB 250Xi instrument). Fourier transform infrared (FT-IR) spectra are recorded on a Nicolet 6700 spectrometer. N₂ sorption isotherms are measured at 77 K using ASAP 2010 analyzer, after the samples are degassed in a vacuum at 120 °C for 12 h. The specific surface area of the materials is calculated using Brunauer-Emmett-Teller (BET) model.

1.4 Electrochemical measurements

1.4.1 Electrode preparation. The catalyst ink is prepared by dispersing the catalyst (43 mg) in Nafion[®] solution (5.0 wt% water solution) dispersion solution in 3 mL ethanol-DI water solution (ethanol : DI water = 1:1)via sonication for 30 min to form a homogeneous suspension. Then, 2 μ L of the catalyst ink is pipetted onto the glassy carbon rotating disk electrode (RDE, 0.071 cm²) for five times and dried at room temperature. The resulting electrode served as a working electrode.

1.4.2 Electrocatalytic testing. Electrochemical measurements are conducted with a CHI660e electrochemical working station (CH Instrument) at room temperature in O_2 saturated 0.1 M KOH solution. A typical three-electrode system was employed, using a glass carbon RDE covered by catalyst as working electrode, a platinum foil as counter electrode, and a saturated calomel electrode (SCE) as the reference electrode as reference electrode. The catalyst loaded working electrode is cycled by cyclic voltammetry (CV) at a scan rate of 10 mV s⁻¹, until stabilized current is obtained. RDE measurements are performed by linear sweep voltammetry (LSV) at a scan rate of 10 mV s⁻¹ with various rotating speeds from 400 to 2500 rpm. The electron transfer number (n) per oxygen molecule in an ORR process is calculated by the Koutecky-Levich (K-L) equation:

(1)
$$J^{-1} = J_k^{-1} + (B\omega^{1/2})^{-1}$$

(2)
$$B = 0.2nF(D_0)^{2/3}v^{-1/6}C_0$$

where J is the measured current density during ORR, J_{k} is the kinetic current density, ω is the electrode rotating angular velocity ($\omega = 2\pi N$, N is the linear rotation speed), *B* is the slope of K-L plots, *n* represents the electron transfer number per oxygen molecule, *F* is the Faraday constant ($F = 96485 \ C \ mol^{-1}$), D_0 is the diffusion coefficient of O₂ in 0.1 _M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), *v* is the kinetic viscosity (0.01 $cm^2 \text{ s}^{-1}$), C_0 is the bulk concentration of O₂ ($1.2 \times 10^{-3} \text{ mol L}^{-1}$). The constant 0.2 is adopted when the rotation speed is expressed in rpm.

1.4.3 Liquid Zn–air battery. The measurements of rechargeable Zn-air batteries are performed on home-built electrochemical cells. All data are collected from the as-fabricated cell with a CHI 760D (CH Instruments, Inc., Shanghai, China) electrochemical workstation at room temperature. Briefly, zinc foil is used as anode and catalysts loaded on the gas diffusion layer (Nafion-coated carbon fiber paper with a geometric area of 1.0 cm², catalyst loading amount of 2.0 mg cm⁻²) used as the air cathode. For comparison, the rechargeable battery is also made with Pt/C serving as the noble-metal cathode. The electrolyte was 6.0 M KOH and 0.2 M zinc acetate solution.

1.4.4 All-solid-state Zn-air battery. A polished zinc foil is used as anode. The gel polymer electrolyte is prepared as follow: polyvinyl alcohol (PVA, 2 g) powder is undergone a high-temperature processing at 90 °C under stirring. After PVA form a uniform gel state, 18 M KOH (0.1 mL) is added. Then, the solution is poured onto a glass plate to form a thin film. The film is then freezed in a freezer at -3 °C for 1 h, and then thawed at room temprature. Then, the as-prepared catalyst and zinc foil are placed on the two sides of PVA gel, followed by pressed Ni foam as current collector.

2. Supplementary Figures



Fig. S1 (a) XRD pattern and (b, c) SEM images of $CoMn_2O_4/N$ -CNTs. Six diffraction peaks are detected, matching well with the lattice planes of the $CoMn_2O_4$. In addition, the graphitic carbon diffraction peak derived from the CNTs is also detected (PDF#41-1487).



Fig. S2 (a) N_2 adsorption-desorption isotherms and (b) corresponding pore distribution curves of CoMn₂O₄/N-CNTs and CoMn₂O₄.



Fig. S3 (a) XRD pattern and (b, c) SEM images of MnCo₂O₄/N-CNTs



Fig. S4 (a) XRD pattern and (b, c) SEM images of Mn₃O₄/N-CNTs.



Fig. S5 (a) XRD pattern and (b, c) SEM images of Co₃O₄/N-CNTs.



Fig. S6 (a, b) Photographs of pristine CNTs and CoMn₂O₄/N-CNTs distributed in the aqueous solution. These kinds of oxygen-contained groups can be verified by the Tyndall effect: owning to the hydrophillic nature of oxygen-contained groups, the oxidized CNTs can well-disperse in the aqueous solution for a long time, as evidenced by the Tyndall light scattering under laser irradiation; nevertheless, the commercial CNTs without the hydrophilic group are unstable and more inclined to precipitate.



Fig. S7 FT-IR spectra of pristine CNTs and $CoMn_2O_4/N$ -CNTs.



Fig. S8 C 1s XPS spectra of $CoMn_2O_4/N$ -CNTs.



Fig. S9 LSV curves and Tafel slopes for the Co-Mn catalysts and Co-Mn-Au catalysts. In addition to Mn^{3+} ions as a primary factor governing ORR activity, the covalency of the Mn–O bond is another influence on the ORR activity since the Mn–O hybridization can mediate electron transfer to oxygen. Therefore, the stabilization of Mn–O bond is crucial for the catalyst. In this work, Co ions are considered as basic metal ions influencing the ORR catalytic activity of the Mn ions. According to the XPS analyses, Co ions with low valence state in CoMn₂O₄/N-CNTs possess stronger basicity than the one with high valence state in MnCo₂O₄/N-CNTs. Consequently, for CoMn₂O₄/N-CNTs,

the electron cloud of Co²⁺ ions with larger radius conjugate the molecular orbital of Mn–O, consolidating the Mn–O bond. It is well known that Au possesses a strong electronegativity to promote the valence state of the metal ions which intimately contact with Au. Therefore, if the conclusion in the manuscript is correct, Mn₃O₄/Au/N-CNTs with high valence state of Mn ions is supposed to possess an improved ORR performances. As expected, after doping Au, the ORR performance of Mn₃O₄/Au/N-CNTs (Fig. S9a, S9b) enhances with the increased valence state of Mn ion (Fig. S10a), demonstrating Mn³⁺ ions are the main ORR catalytic sites. The Au doping probe test further confirm the role of Co ions. Accompanied with the increased valence state of Co ion (Fig. S10b) after the doping of Au, the increased amount of acidic Co ions in CoMn₂O₄/Au/N-CNTs generates a dramatic degradation of the ORR activity (Fig. S9c, S9d), illustrating the significant function of Co²⁺ ions. On the other hand, since Co³⁺ is served as the substrate to interact with Mn ions in MnCo₂O₄/N-CNTs, the transformation from Co^{2+} to Co^{3+} (Fig. S10b) after the Au doping has little impact on the ORR performance of MnCo₂O₄/Au/N-CNTs (Fig. S9e, S9f). Therefore, from another point of view, this result also illustrates the indispensable role of Co²⁺ ions. In conclusion, in terms of Mn-based materials, Mn³⁺ ion is the mainly catalytic sites for ORR reaction, while doping electron-rich ions would further promote the ORR performance by stabilizing the covalency of the Mn–O bond.



Fig. S10 (a) Mn 3s XPS spectra and (b) Co 2p XPS spectra of $CoMn_2O_4/N$ -CNTs, MnCo₂O₄/N-CNTs and Mn₃O₄/N-CNTs.



Figure S11. (a) LSVs with different scanning rates for CoMn₂O₄/N-CNTs. (b) The

corresponding Koutecky-Levich plots for CoMn₂O₄/N-CNTs.



Figure S12. C 1s XPS spectra of CoMn₂O₄/N-CNTs, MnCo₂O₄/N-CNTs, Mn₃O₄/N-CNTs and Co₃O₄/N-CNTs. Influenced by the N atoms, the electron cloud of the connected carbon atoms migrates out of the carbon center owning to the strong electronegativity. Therefore, the activated carbon atoms with the electropositive property are capable of absorbing the oxygen molecules and catalyzing them into OH⁻.



Figure S13. N 1s XPS spectra of CoMn₂O₄/N-CNTs.



Figure S14. Zn–air battery performance in aqueous electrolyte with $CoMn_2O_4/N$ -CNTs acting as the air cathode in comparison with the coupled noble metal Pt/C catalyst. (a) The Schematic representation of Zn-air battery; (b) Open circuit plots; (c) Discharging polarization (*V*–*j*) curves and the corresponding power plots; (d) Specific discharging capacity plots at different current density; (e) Energy density plots at different current density; (f) Galvanostatic discharging measurements at different current density.



Figure S15. Galvanostatic discharging test of Zn-air battery with $CoMn_2O_4/N$ -CNTs

cathode at different current density.



Figure S16. Discharging polarization (*V*–*j*) curves and the corresponding power plots.