Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Optimization of Cobalt/Nitrogen embedded Carbon Nanotube as Efficient Bifunctional Oxygen Electrode for Rechargeable Zinc Air Battery

Junhua Song, Chengzhou Zhu*, Shaofang Fu, Yang Song, Dan Du and Yuehe Lin*
School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA.

1. Analysis of electron transfer number

The number of electrons transferred in the oxygen reduction reaction is calculated from Koutecky–Levich plots (J^{-1} vs. $\omega^{-1/2}$) at range of electrode potentials. The calculation can be carried out using the following Koutecky–Levich equation: 1) $1/J = 1/J_L + 1/J_K = 1/B\omega^{1/2} + 1/J_K$, 2) $B = 0.62nFC_0(D_0)^{2/3}v^{-1/6}$, 3) $J_K = nFkC_0$. Here J, J_L and J_K are the measured current density, diffusion limiting current density and kinetic current density, respectively. ω is the rotation grade in rad s^{-1}. n is the overall electron transfer number in ORR, F is the Faraday constant and taken as 96485 C mol^{-1}. D_0 is the diffusion coefficient (1.9×10^{-5} cm^2s^{-1}), v is the kinetic viscosity of the electrolyte (0.01) and C_0 is the bulk concentration of oxygen (1.2×10^{-3} mol L^{-1}). k is the electron-transfer constant. The number of transferred electrons can be calculated based through equation 1) to 3).

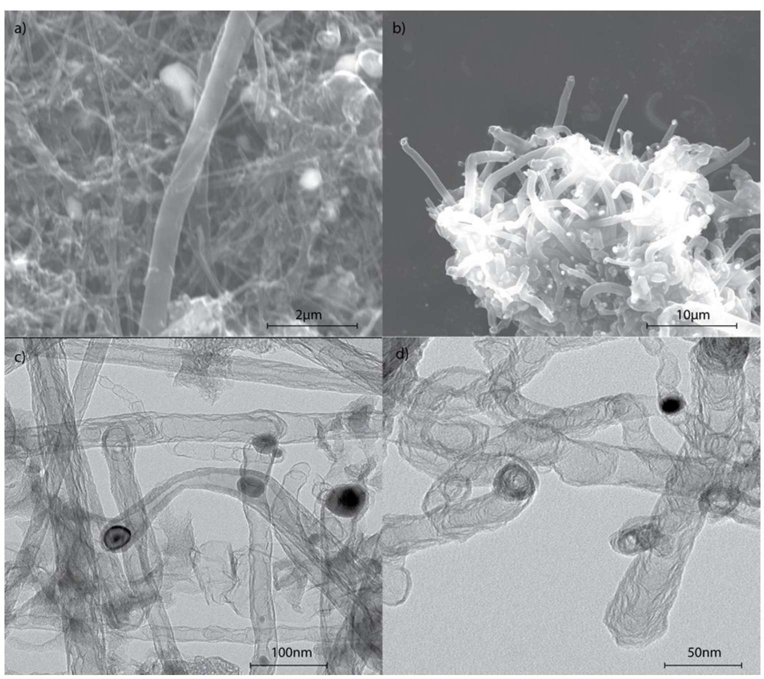

Fig. S1 a) Transmission electron microscope (TEM) characterization of FeNCN-44. b) Scanning electron microscope (SEM) image of NiNCN-22. c) Picture of FeNCN-44 under TEM survey. d) TEM image of NiNCN-22

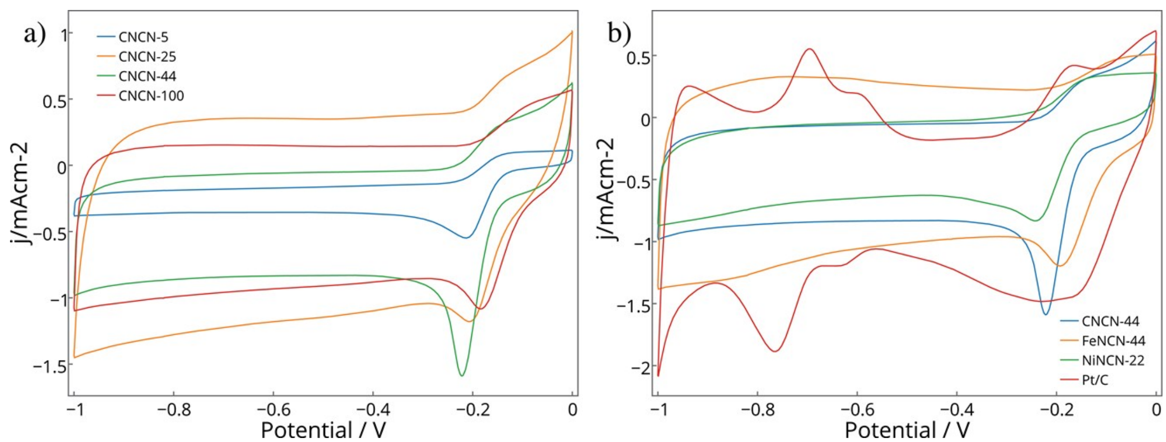

Fig. S2 Cyclic Voltammetry (CV) plot of CNCN-5, CNCN-25, CNCN-44, CNCN-100, FeNCN-44, NiNCN-22 and commercial Pt/C at a scan rate of 50 mV/s in 0.1M KOH electrolyte. a) CV plots of different CNCN catalysts in O_2-saturated electrolyte. b) Comparing CV plots of CNCN-44 FeNCN-44, NiNCN-22 and Pt/C in O O_2-saturated electrolyte.

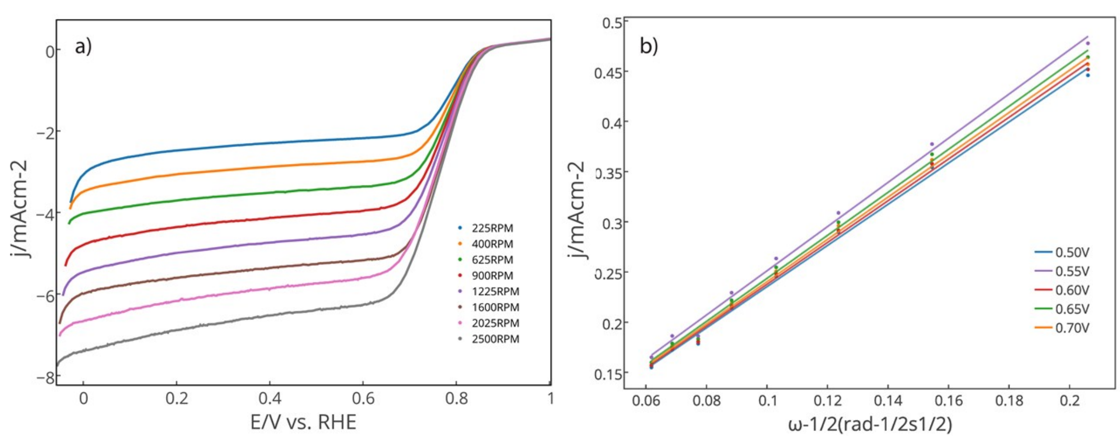

Fig. S3 a) Linear Sweep Voltammetry plots of optimized CNCN-44 with different rotation rate in 0.1M KOH electrolyte at a scan rate of 10 mV s^{-1}. b) Koutecky–Levich (K–L) plots of CNCN-44 obtained from the rotating disk electrode (RDE) results at different potentials.

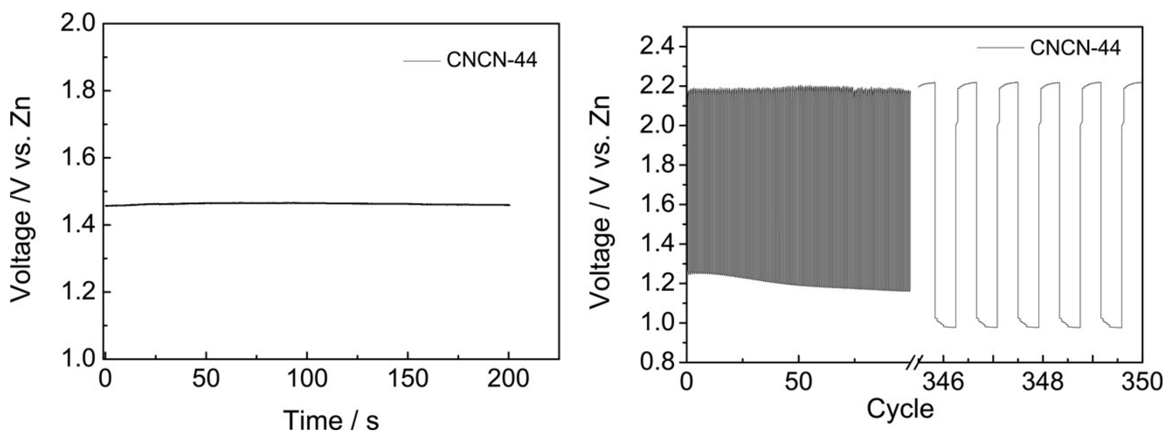

Fig. S4 a) Open circuit potential of CNCN-44 showing good electron conductivity of the prepared catalyst. c) Long-term cycling performance of CNCN-44 operated at 5 mA cm^{-2} with 4 minutes charge-discharge per cycle.

Table S1. Comparison of bifunctional electroactivity of CNCN-44 to various reported precious and non-precious catalysts

Catalyst	E_{ORR}/V j=-3mAcm^{-2}	E_{OER}/V j=10mAcm^{-2}	ΔE/V (E_{OER}- E_{ORR})	Ref
$NiCo_2O_4$	0.75	1.72	0.97	S1
NCo-A_1	0.78	1.62	0.89	S2
CoxOy/NC	0.81	1.70	0.89	20
Co/N-C-800	0.74	1.60	0.86	18
CoS_2(400)/N,S-GO	0.79	1.61	0.82	S3
N-graphene/CNT	0.69	1.65	0.96	9
20 wt% Ir/C	0.69	1.61	0.92	19
CNCN-44	0.80	1.61	0.81	This work

References:

S1. Jin, C.; Lu, F. L.; Cao, X. C.; Yang, Z. R.; Yang, R. Z., *J. Mater. Chem. A,* 2013, ***1***, 12170-12177.

S2. Prabu, M.; Ketpang, K.; Shanmugam, S., *Nanoscale,* 2014, ***6***, 3173-3181.

S3. Ganesan, P.; Prabu, M.; Sanetuntikul, J.; Shanmugam, S., *ACS Catal.,* 2015, ***5***, 3625-3637.