

## Supplementary Materials

# High-Density Cobalt Nanoparticles Encapsulated with Nitrogen-Doped Carbon Nanoshells as a Bifunctional Catalyst for Rechargeable Zinc-Air Battery

Shuqi Liang and Ce Liang \*

Key Laboratory of Automobile Materials, Ministry of Education, and College of Materials Science and Engineering, Jilin University, Changchun 130025, China; lsqjlu@163.com

\* Correspondence: liangce@jlu.edu.cn; Tel.: +86-431-8509-5170

**Table 1.** Comparison of bifunctional oxygen electrode activity data for different catalysts.

| Catalysts                               | Loading<br>( $\mu\text{g}\cdot\text{cm}^{-2}$ ) | $E_{\text{ORR}}/\text{V}$<br>( $I = -3 \text{ mA}\cdot\text{cm}^{-2}$ ) | $E_{\text{OER}}/\text{V}$<br>( $I = 10 \text{ mA}\cdot\text{cm}^{-2}$ ) | $\Delta E/\text{V}$<br>( $E_{\text{OER}} - E_{\text{ORR}}$ ) | Electrolyte | Source    |
|-----------------------------------------|-------------------------------------------------|-------------------------------------------------------------------------|-------------------------------------------------------------------------|--------------------------------------------------------------|-------------|-----------|
| Pt/C                                    | 200                                             | 0.82                                                                    | 1.86                                                                    | 1.04                                                         | 0.1 M KOH   | ref. [1]  |
| IrO <sub>2</sub>                        | 210                                             | 0.29                                                                    | 1.70                                                                    | 1.41                                                         | 0.1 M KOH   | ref. [2]  |
| 20% Ir/C                                | 28                                              | 0.69                                                                    | 1.61                                                                    | 0.92                                                         | 0.1 M KOH   | ref. [3]  |
| RuO <sub>2</sub>                        | 210                                             | 0.37                                                                    | 1.64                                                                    | 1.27                                                         | 0.1 M KOH   | ref. [2]  |
| 20% Ru/C                                | 28                                              | 0.61                                                                    | 1.62                                                                    | 1.01                                                         | 0.1 M KOH   | ref. [3]  |
| Co-N/C 800                              | 240                                             | 0.78                                                                    | 1.74                                                                    | 0.96                                                         | 0.1 M KOH   | ref. [4]  |
| Co/N-C-800                              | 250                                             | 0.74                                                                    | 1.60                                                                    | 0.86                                                         | 0.1 M KOH   | ref. [5]  |
| Fe@N-C                                  | ~311                                            | 0.83                                                                    | 1.71                                                                    | 0.88                                                         | 0.1 M KOH   | ref. [6]  |
| Fe/N-CNTs                               | 200                                             | 0.81                                                                    | 1.75                                                                    | 0.94                                                         | 0.1 M KOH   | ref. [1]  |
| CNCN-44                                 | 200                                             | 0.80                                                                    | 1.61                                                                    | 0.81                                                         | 0.1 M KOH   | ref. [7]  |
| (Ni,Co)/CNT                             | 240                                             | 0.74                                                                    | 1.60                                                                    | 0.87                                                         | 0.1 M KOH   | ref. [8]  |
| meso-Co <sub>3</sub> O <sub>4</sub> -35 | 100                                             | 0.61                                                                    | 1.64                                                                    | 1.03                                                         | 0.1 M KOH   | ref. [9]  |
| FeCo@NC-750                             | 800                                             | ~0.79                                                                   | 1.49                                                                    | 0.70                                                         | 0.1 M KOH   | ref. [10] |
| Ni <sub>3</sub> Fe/N-C                  | 130                                             | 0.78                                                                    | 1.62                                                                    | 0.84                                                         | 0.1 M KOH   | ref. [11] |
| N-graphene/CNT                          | ~424                                            | 0.69                                                                    | 1.65                                                                    | 0.96                                                         | 0.1 M KOH   | ref. [12] |
| m-NiFe/CNx                              | 200                                             | 0.76                                                                    | 1.59                                                                    | 0.83                                                         | 0.1 M KOH   | ref. [13] |
| CoFe <sub>2</sub> O <sub>4</sub> /rGO   | 1006                                            | 0.73                                                                    | 1.71                                                                    | 0.98                                                         | 0.1 M KOH   | ref. [14] |
| Co-N/C-800                              | 100                                             | 0.84                                                                    | 1.64                                                                    | 0.80                                                         | 0.1 M KOH   | this work |

**Table 2.** Comparison of the performances of rechargeable Zn–air battery for different catalysts.

| Catalysts                               | Loading<br>(mg·cm <sup>-2</sup> ) | Per Cycle<br>(min) | Cycle<br>Time<br>(h) | Fluctuation of<br>Discharge<br>Potential (E <sub>DP</sub> )<br>(V, initial/end) | Fluctuation of<br>Charge<br>Potential (E <sub>CP</sub> )<br>(V, initial/end) | Current<br>Density<br>(mA·cm <sup>-2</sup> ) | Source    |
|-----------------------------------------|-----------------------------------|--------------------|----------------------|---------------------------------------------------------------------------------|------------------------------------------------------------------------------|----------------------------------------------|-----------|
| NCNT/CoO-NiO-NiCo                       | 0.53                              | 10                 | 17                   | ~1.11/1.06                                                                      | ~2.03/1.97                                                                   | 20                                           | ref. [15] |
| Fe@N-C                                  | 2.2                               | 10                 | 16.7                 | 1.25/1.11                                                                       | 1.95/1.97                                                                    | 10                                           | ref. [6]  |
| Co-PDA-C                                | 1                                 | 60                 | 500                  | 1.21/1.01                                                                       | 2.15/2.18                                                                    | 2                                            | ref. [16] |
| CoMn <sub>2</sub> O <sub>4</sub> /N-rGO | -                                 | 10                 | ~16.7                | ~1.09/1.01                                                                      | ~1.77/1.89                                                                   | 20                                           | ref. [17] |
| Ni <sub>3</sub> Fe/N-C sheets           | -                                 | 240                | 420                  | ~1.17/1.05                                                                      | ~1.98/2.06                                                                   | 10                                           | ref. [11] |
| FeCo@NC-750                             | 1                                 | 10                 | 20                   | ~1.21/1.14                                                                      | ~1.96/2.00                                                                   | 10                                           | ref. [10] |
| NiCo <sub>2</sub> O <sub>4</sub> -CNTs  | 2                                 | 10                 | 40                   | ~1.30/1.22                                                                      | ~2.08/2.17                                                                   | 10                                           | ref. [18] |
| Co-N/C-800                              | 1                                 | 60                 | 100                  | 1.21/1.12                                                                       | 1.50/1.51                                                                    | 10                                           | This work |

## Reference

1. Y. Liu, H. Jiang, Y. Zhu, X. Yang, C. Li, Transition metals (Fe, Co, and Ni) encapsulated in nitrogen-doped carbon nanotubes as bi-functional catalysts for oxygen electrode reactions, *J. Mater. Chem. A.*, 4 (2016) 1694–1701.
2. A. Aijaz, J. Masa, C. Rösler, W. Xia, P. Weide, A.J.R. Botz, R.A. Fischer, W. Schuhmann, M. Muhler, Co@Co<sub>3</sub>O<sub>4</sub> Encapsulated in Carbon Nanotube-Grafted Nitrogen-Doped Carbon Polyhedra as an Advanced Bifunctional Oxygen Electrode, *Angew. Chemie Int. Ed.*, 55 (2016) 4087–4091.
3. Y. Gorlin, T.F. Jaramillo, A bifunctional nonprecious metal catalyst for oxygen reduction and water oxidation, *J. Am. Chem. Soc.*, 132 (2010) 13612–13614.
4. W. Hu, Q. Wang, S. Wu, Y. Huang, Facile one-pot synthesis of a nitrogen-doped mesoporous carbon architecture with cobalt oxides encapsulated in graphitic layers as a robust bicatalyst for oxygen reduction and evolution reactions, *J. Mater. Chem. A.*, 4 (2016) 16920–16927.
5. Y. Su, Y. Zhu, H. Jiang, J. Shen, X. Yang, W. Zou, J. Chen, C. Li, Cobalt nanoparticles embedded in N-doped carbon as an efficient bifunctional electrocatalyst for oxygen reduction and evolution reactions, *Nanoscale*, 6 (2014) 15080–15089.
6. J. Wang, H. Wu, D. Gao, S. Miao, G. Wang, X. Bao, High-density iron nanoparticles encapsulated within nitrogen-doped carbon nanoshell as efficient oxygen electrocatalyst for zinc–air battery, *Nano Energy*, 13 (2015) 387–396.
7. J. Song, C. Zhu, S. Fu, Y. Song, D. Du, Y. Lin, Optimization of cobalt/nitrogen embedded carbon nanotubes as an efficient bifunctional oxygen electrode for rechargeable zinc–air batteries, *J. Mater. Chem. A.*, 4 (2016) 4864–4870.
8. N. Ma, Y. (Alec) Jia, X. Yang, X. She, L. Zhang, Z. Peng, X. Yao, D. Yang, Seaweed biomass derived (Ni,Co)/CNT nanoaerogels: efficient bifunctional electrocatalysts for oxygen evolution and reduction reactions, *J. Mater. Chem. A.*, 4 (2016) 6376–6384.
9. Y.J. Sa, K. Kwon, J.Y. Cheon, F. Kleitz, S.H. Joo, Ordered mesoporous Co<sub>3</sub>O<sub>4</sub> spinels as stable, bifunctional, noble metal-free oxygen electrocatalysts, *J. Mater. Chem. A.*, 1 (2013) 9992.
10. P. Cai, S. Ci, E. Zhang, P. Shao, C. Cao, Z. Wen, FeCo Alloy Nanoparticles Confined in Carbon Layers as High-activity and Robust Cathode Catalyst for Zn-Air Battery, *Electrochim. Acta*, 220 (2016) 354–362.
11. G. Fu, Z. Cui, Y. Chen, Y. Li, Y. Tang, J.B. Goodenough, Ni<sub>3</sub>Fe-N Doped Carbon Sheets as a Bifunctional Electrocatalyst for Air Cathodes, *Adv. Energy Mater.*, 7 (2017) 1–8.
12. Z. Wen, S. Ci, Y. Hou, J. Chen, Facile one-pot, one-step synthesis of a carbon nanoarchitecture for an advanced multifunctional electrocatalyst, *Angew. Chemie. Int. Ed.*, 53 (2014) 6496–6500.
13. S. Ci, S. Mao, Y. Hou, S. Cui, H. Kim, R. Ren, Z. Wen, J. Chen, Rational design of mesoporous NiFe-alloy-based hybrids for oxygen conversion electrocatalysis, *J. Mater. Chem. A.*, 3 (2015) 7986–7993.
14. W. Bian, Z. Yang, P. Strasser, R. Yang, A CoFe<sub>2</sub>O<sub>4</sub>/graphene nanohybrid as an efficient bi-functional electrocatalyst for oxygen reduction and oxygen evolution, *J. Power Sources*, 250 (2014) 196–203.

15. X. Liu, M. Park, M.G. Kim, S. Gupta, G. Wu, J. Cho, Integrating NiCo Alloys with Their Oxides as Efficient Bifunctional Cathode Catalysts for Rechargeable Zinc-Air Batteries, *Angew. Chemie. Int. Ed.*, **54** (2015) 9654–9658.
16. B. Li, Y. Chen, X. Ge, J. Chai, X. Zhang, T.S.A. Hor, G. Du, Z. Liu, H. Zhang, Y. Zong, Mussel-inspired one-pot synthesis of transition metal and nitrogen co-doped carbon (M/N-C) as efficient oxygen catalysts for Zn-air batteries, *Nanoscale*, **8** (2016) 5067–5075.
17. M. Prabu, P. Ramakrishnan, S. Shanmugam, CoMn<sub>2</sub>O<sub>4</sub> nanoparticles anchored on nitrogen-doped graphene nanosheets as bifunctional electrocatalyst for rechargeable zinc-air battery, *Electrochem. Commun.*, **41** (2014) 59–63.
18. C. Ma, N. Xu, J. Qiao, S. Jian, J. Zhang, Facile synthesis of NiCo<sub>2</sub>O<sub>4</sub> nanosphere-carbon nanotubes hybrid as an efficient bifunctional electrocatalyst for rechargeable Zn-air batteries, *Int. J. Hydrogen Energy*, **41** (2016) 9211–9218.