

Metal-Organic Framework Derived Co-N-C Electrocatalysts for Efficient Hydrogen Evolution in Acid and Alkaline Media

Jiyoung Kim^{1,2}, Beum Jin Park¹, Younghwan Cha², Panpan Dong², Min-Kyu Song^{2,*}, Ho Seok Park^{1,*}

¹*School of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea*

²*School of Mechanical and Materials Engineering, Washington State University, Pullman, United States*

*Presenting author's e-mail: jyoung.kim3@wsu.edu

Introduction

Hydrogen have been attracted great attentions as an efficient energy carrier due to the advantage of high gravimetric energy density and clean use through fuel cells or CO₂ free combustion. Among the various methods to produce the hydrogen, water splitting using hydrogen evolution reaction (HER) coupled with oxygen evolution is considered as an effective way to use renewable energy resources. Considering the demand growth for hydrogen production, it is necessary to develop the cost-competitive non-noble metal catalyst with high activity and durability. Herein, we synthesized the cobalt catalysts supported on the nitrogen-doped carbons derived from metal-organic frameworks (MOF), and examined the HER performance focused on their porous structure.

Materials and Methods

For the synthesis of Co-MOF, Co(NO₃)₂·6H₂O and 2-Methylimidazole were dissolved in alcoholic solvents separately. Above solutions were mixed with stirring for 1 min and kept for 24 h at room temperature. In order to introduce the porous structure, Zn/Co-MOF was also prepared by adding Zn(NO₃)₂·6H₂O in cobalt solution. Co-N-C and porous Co-N-C catalysts were obtained by the pyrolysis of Co-MOF and Zn/Co-MOF at 900 °C for 3 h, respectively.

Results and Discussion

Figure 1. shows the morphology of Co-N-C and porous Co-N-C by SEM and TEM. The pristine polyhedron shapes were maintained well after the pyrolysis of the MOFs. It is observed that cobalt metals were embedded in the carbon structure. The particle size of cobalt in porous Co-N-C is relatively smaller than that of Co-N-C, suggesting the Zn species prevent the aggregation of cobalt metals during the pyrolysis until the Zn evaporation at 900 °C. From the N₂ sorption isotherms (data is not shown), it was also clearly confirmed that the mesoporous structure was discovered in the porous Co-N-C by the removal of Zn species, indicating the critical role of Zn species in forming favourable structure as electrocatalysts.

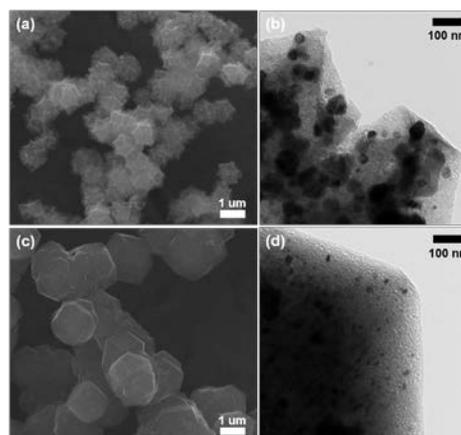


Figure 1 (a) SEM and (b) TEM image of Co-N-C polyhedrons and (c, d) porous Co-N-C.

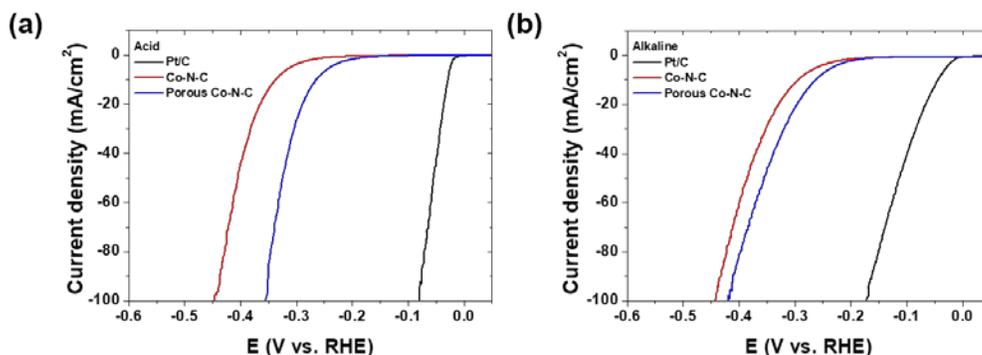


Figure 2 Polarization curves for hydrogen evolution reaction at 2 mV/s in (a) 0.5 M H₂SO₄ and (b) 1 M KOH electrolyte.

The improved electrocatalytic activity of porous Co-N-C is investigated using conventional three-electrode system in acid (0.5 M H₂SO₄) and alkaline (1.0 M KOH) electrolyte shown in **Figure 2**. It could be found that the porous Co-N-C exhibited the better HER activity with a lower overpotential of 265 mV at a current density of 10 mA/cm² than Co-N-C of 338 mV in acid electrolyte. The superiority of porous Co-N-C for HER can be also confirmed in alkaline with an overpotential of 263 mV compared to the Co-N-C of 295 mV, showing the attractive structure of porous Co-N-C as electrocatalysts.

Conclusions

In this study, we present cobalt-embedded electrocatalysts supported on 3D-structured nitrogen-doped carbon (Co-N-C) by simple carbonization of cobalt-based metal-organic framework (MOF), affording improved catalytic performance and durability in both of acid and alkaline media. The porous Co-N-C from Co/Zn hybrid precursor exhibits low overpotential, high current density and remarkable durability for HER compared with the catalyst from single Co-MOF. The electrocatalytic performance for HER was affected by increasing the reaction sites and improving the mass transport by the unique structure, which is formed by evaporation of zinc species during the carbonization.

Acknowledgment

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (no. 2017R1A6A3A11031355)

References

1. F. Safizadeh, E. Ghali, G. Houlachi (2015). Electrocatalysis developments for hydrogen evolution reaction in alkaline solutions – a review. *International Journal of Hydrogen Energy* 40, 256-274
2. S. Dang, Q. L. Zhu, Q. Xu (2017). Nanomaterials derived from metal-organic frameworks. *Nature Reviews Materials* 3, 17075
3. B. You, N. Jiang, M. Sheng, W. S. Drisdell, J. Yano, Y. Sun (2015). Bimetal-organic framework self-adjusted synthesis of support-free nonprecious electrocatalysts for efficient oxygen reduction. *ACS Catalysis* 5, 7068-7076