Journal of Power Sources 380 (2018) 174–184

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Facile preparation of efficient electrocatalysts for oxygen reduction reaction: One-dimensional meso/macroporous cobalt and nitrogen Co-doped carbon nanofibers

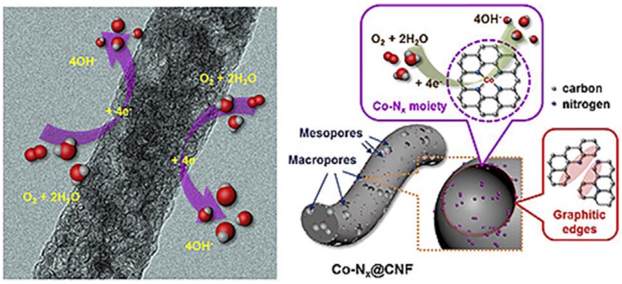
Ki Ro Yoon[a], Jinho Choi[b], Su-Ho Cho[a], Ji-Won Jung[a], Chanhoon Kim[a], Jun Young Cheong[a], Il-Doo Kim[a,*]

[a] *Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea*
[b] *School of Freshman, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea*

HIGHLIGHTS

- Co and N co-doped carbon nanofibers have been prepared by electrospinning method.
- Meso/macroporous carbon nanofibers possessed numerous graphite flakes and Co-N_x sites.
- Developed catalyst exhibit excellent catalytic activity and high stability towards ORR.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Cobalt nanoparticles
Carbon nanofibers
Oxygen reduction reaction
Electrocatalysts
Electrospinning

ABSTRACT

Efficient electrocatalyst for oxygen reduction reaction (ORR) is an essential component for stable operation of various sustainable energy conversion and storage systems such as fuel cells and metal-air batteries. Herein, we report a facile preparation of meso/macroporous Co and N co-doped carbon nanofibers (Co-N_x@CNFs) as a high performance and cost-effective electrocatalyst toward ORR. Co-N_x@CNFs are simply obtained from electrospinning of Co precursor and bicomponent polymers (PVP/PAN) followed by temperature controlled carbonization and further activation step. The prepared Co-N_x@CNF catalyst carbonized at 700 °C (Co-N_x@CNF700) shows outstanding ORR performance, i.e., a low onset potential (0.941 V) and half wave potential (0.814 V) with almost four-electron transfer pathways ($n = 3.9$). In addition, Co-N_x@CNF700 exhibits a superior methanol tolerance and higher stability (> 70 h) in Zn-air battery in comparison with Pt/C catalyst (~ 30 h). The outstanding performance of Co-N_x@CNF700 catalysts is attributed to i) enlarged surface area with bimodal porosity achieved by leaching of inactive species, ii) increase of exposed ORR active Co-N_x moieties and graphitic edge sites, and iii) enhanced electrical conductivity and corrosion resistance due to the existence of numerous graphitic flakes in carbon matrix.

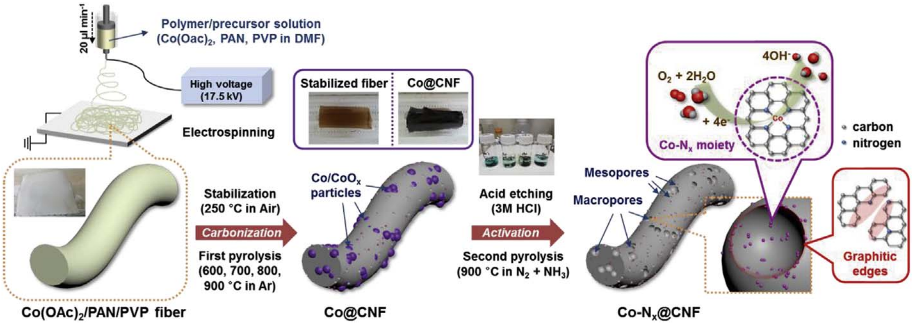
1. Introduction

Clean and sustainable energy storage and conversion technologies have attracted huge attention due to the ever-growing concerns about global warming and insistent demands for renewable energy. Among various innovative approaches, oxygen based electrochemistry

---

* Corresponding author.
E-mail address: idkim@kaist.ac.kr (I.-D. Kim).

https://doi.org/10.1016/j.jpowsour.2018.01.076
Received 29 September 2017; Received in revised form 22 January 2018; Accepted 26 January 2018



Scheme 1. Schematic illustration of the preparation procedure of Co-N_x@CNF catalysts for ORR.

involving electrochemical conversion reactions between oxygen and water is a conceptually simple method to provide or store electrical energy efficiently via reversible chemical bonding [1]. Oxygen reduction reaction (ORR) is of the great importance in these electrochemical technologies especially for fuel cells and metal-air batteries [2,3]. However, sluggish kinetic of ORR always requires the use of electrocatalysts, and the unacceptable high cost of platinum-group metal (PGMs) catalysts hinder the wide use of these technologies in the large scale applications such as electric vehicles [4]. In order to address this issue, the extensive efforts have been devoted to develop affordable and highly efficient non-PGM catalysts, such as transition metal-carbon hybrids [5,6] and non-metal carbon based catalysts [1,7–9].

An increasing number of studies have focused on M-N/C class in which transition metals (M = Co, Fe, Mn) and nitrogen (N) are co-doped into carbon matrix, ever since Jasinski reported the ORR activity on cobalt phthalocyanine catalyst [10]. General approaches to prepare the M-N/C catalysts involve the adsorption of macrocycles (M-phthalocyanine [11] or M-phorphyrin [12]) on carbon supports or the physical mixing of individual N-containing organic precursors (polyaniline [13], polyacrylonitrile (PAN) [14], and polypyrrole [15]) and M precursors followed by pyrolysis in an inert or NH_3 atmosphere. More recently, metal-organic frameworks (MOFs) driven carbon-based catalysts also have been demonstrated as ORR catalysts due to the simultaneous incorporation of carbon and metals within the framework and the high surface area of MOF structures [16,17]. However, these catalytic groups still have some remaining issues to be overcome, which include the poor intrinsic catalytic activity of a single active site (mostly comes from the N-coordinated M moiety, M-N_x) compared with PGMs, low volumetric active site density due to the difficulty in controlling porosity and structure, poor electron transfer to the active sites, and rapid loss of initial performance due to the low electrochemical stability [18]. To this end, the rational design of optimal carbon-supported electrocatalysts by meeting following criteria is required: i) sufficient and uniform active sites with minimal inactive volume; ii) high graphitic degree of carbon matrix to facilitate electron transfer and resist corrosion; and iii) large surface area and suitable pore size to allow facile mass transport and gas diffusion.

As an one-dimensional (1D) carbon support as well as catalytic material, carbon nanofiber (CNF), particularly prepared by electrospinning technique, has also been widely investigated in various electrocatalysis owing to its simplicity in producing composite nanofibers and elemental doping by adding adequate chemical resources, high aspect ratio enabling the formation of conductive network as supports, and high flexibility of creating various morphological features [19,20]. Especially, PAN-driven CNF, which has a turbostratic structure with many quasi-ordered graphitic domains along the axial direction of fibers, contains naturally doped N owing to the carbonization of nitrile groups ($-C\equiv N$) comprising of PAN. These features lead to the formation of sp^2 carbon structures and different N-functionalities after carbonization [21–23]. Notably, porosity of CNFs can be easily modulated through the phase separation behavior of two mixed polymers that takes place during electrospinning [24–27]. For instance, electrospinning of immiscible bicomponent polymers (e.g., polyvinylpyrrolidone (PVP)/PAN [28] or poly (styrene-acrylonitrile)/PAN [29,30]) has been intended to accelerate the dispersion of one in the matrix of the other and generate selective inter-fiber pores by removal of the dispersed phase domains, leading to high surface area and low volumetric density of fibers.

Besides the metal-free CNFs, various M (Fe [31–35] and Co [14,36,37]) and N co-doped CNFs (M-N/CNFs) have been prepared by calcining electrospun M-precursor/polymer composite fibers, which exhibit excellent electrocatalytic performance for ORR. For instance, Jeong et al. prepared Fe particles embedded N doped CNFs by electrospinning and subsequent carbonization, and they found out that the additional water vapor treatment can enhance the ORR activity due to the increase of surface Fe-N_x sites [31]. Shang et al. reported Co nanoparticles encapsulated in N doped CNFs obtained by electrospinning and pyrolysis at various temperatures and demonstrated their ORR activity in alkaline medium [36]. Moreover, Wang et al. synthesized Co-N-P doped CNFs by electrospinning of urea and triphenylphosphine added polymer solutions, possessing bifunctional catalytic activity toward both ORR and hydrogen evolution reaction (HER) [37]. However, these reported catalysts still contained inorganic particles in the CNFs, which occupied inactive volume and mass of catalysts. Furthermore, the creation of surface ORR active sites by introducing porous structure or increasing the number of active species should be necessary for further improvement in electrocatalytic performance of these 1D M-N/CNFs.

In this work, we report a facile preparation of Co and N co-doped CNF based catalysts (denoted as Co-N_x@CNF) with enhanced ORR activity by using simple electrospinning, carbonization and further activation process. Scheme 1 shows the schematic illustration of the entire procedure for preparing Co-N_x@CNF catalysts. The as-spun fibers obtained from the electrospinning of two polymers (PVP/PAN) and cobalt acetate ($Co(OAc)_2$) in *N,N*-dimethylformamide (DMF) solution were pyrolyzed at high temperatures (600, 700, 800 and 900 °C). Co particles with different sizes embedded in CNFs (denoted as Co@CNFs) were then obtained. As an important processing step to activate Co@CNF samples, the inactive Co-based species were leached by hydrochloric acid (HCl) to provide bimodal porosity and the products were post-annealed to expand the ORR active species at 900 °C in N_2 atmosphere with NH_3. The microstructural evolution related with unique meso/macroporous 1D structure, formation of Co-N_x moieties, and graphitic edges of Co-N_x@CNFs were elaborately analyzed by physical/chemical characterizations. The electrochemical ORR performances of prepared catalysts were investigated by using cyclic voltammetry (CV), linear sweep voltammetry (LSV), and rotating disk electrode (RDE) technique. In addition, the long-term stabilities of catalysts were characterized in methanol added half-cell system as well as reversible Zn-air battery cells. We found that the ORR activity of catalysts was remarkably improved by post activation process, benefiting from their highly exposed accessible surface area for facile mass transport of O_2, intimately