



# Effect of transition metal induced pore structure on oxygen reduction reaction of electrospun fibrous carbon



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## ABSTRACT

Although significant progress has been made in the development of carbon-based oxygen reduction reaction catalysts in alkaline media, it is still needed to do relevant investigation of experimental factors that could influence the electrocatalytic activity of alternative electrocatalysts. In this study, we report the effect of transition metals placed into/onto nitrogen doped carbon nanofibers on the ORR performance. We demonstrated various behaviors of oxygen reduction reaction reactivity depending on embedded transition metals. Detailed physicochemical analysis showed that different surface area and pore structure were formed according to a number of metals and these structural varieties were resulted from difference in catalytic graphitization phenomenon.

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## 1. Introduction

Since the fossil fuel causes a lot of problems such as environmental pollution, and exhaustion of energy, the demand of developing alternative energy source and energy devices has been continuously increased over the last few years. In particular, electrochemical energy cells such as fuel cell and metal-air battery are getting attraction due to a lot of advantages [1]. In these electrochemical applications, the oxygen related reaction, especially oxygen reduction reaction (ORR) plays a crucial role since it can determine the performance of the electrochemical energy devices [1,2]. To date, platinum (Pt) is well known as the best ORR catalyst due to moderate adsorption and desorption strength of oxygen molecule but it is too expensive to be commercially utilized in various applications. Therefore, the great efforts have been devoted to develop superb non-Pt catalysts and it is regarded as the most overriding issue in the electrochemical technologies.

Of late, there are two approaches to develop the alternative ORR catalyst: one is the minimization of the Pt amount and the other is exploring inexpensive materials with the comparable activity to Pt [1,3]. In the latter, the optimal combination of a number of

transition metals and carbon materials such as carbon nanofiber (CNF), carbon nanotube (CNT), graphene, porous carbon could be ORR active catalysts [3–11]. In particular, heteroatom doped carbon provides superb ORR activity in spite of the absence of metal compounds [12–17]. The reason of enhanced ORR activity in heteroatom doped carbon is reported that adding of electronegative N atoms might reduce the density of C atoms that are adjacent to N and the positively charged C atoms makes to facilitate the O<sub>2</sub> absorption. Subsequently, an increase of the local density of states around the Fermi level of N-doped graphitic carbons facilitates a charge transfer to the adsorbed oxygen molecule, which reduces the dissociation energy barrier [18,19].

As mentioned above, it seems to be certain that heteroatom doped carbon based catalysts might provide the similar activity with Pt based catalyst. However, there are still several issues that should be clearly understood. For instance, the newly developed non-Pt catalyst is mostly synthesized based on a number of experiments without controlled conditions. Thus, it is needed that systematical approaches should be considered for both rational design and developing of innovating ORR catalyst. Moreover, it is known that different transition metals make variety of structural changes due to different mechanism in catalytic graphitization phenomena and they could result in the formation of different density or coordination of Me-N<sub>x</sub> moieties [19–22]. Hence, unravelling the effect of transition metal on the ORR activity is absolutely needed to maximize the level of state of the art in heteroatom doped carbon for ORR catalysts.

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In this study, we tried to introduce the various transition metal precursors, especially iron triad elements (Fe, Co, Ni), in electrospinning process as a facile one-step synthesis method [23]. Furthermore, we examined ORR activity with following aspects: pore structure in carbon, transition metal residues, and the heteroatom content.

## 2. Experimental methods

The transition metal containing electrospun carbon nanofibers (TM-CNFs) were prepared by electrospinning the metal precursor containing polymer solution and subsequent heat treatment at high temperature. 4 g polyacrylonitrile (PAN) was dissolved in 36 g N,N-dimethylformamide (DMF) at 60–80 °C for around 3 h to prepare the polymer solution. After PAN was completely mixed in DMF, the polymer solution was mixed with the different kind of metal precursors, Fe(III) acetylacetonate, Co(III) acetylacetonate, and Ni(II) acetylacetonate. The weight of metal precursors was 1.2 g in metal precursor containing polymer solution (Me-PAN) that could load around 20 wt% of transition metal in CNF. For electrospinning of the Me-PAN solution, it was supplied at a flow rate of 5 ml h<sup>-1</sup> for 6 h with 5 multi-nozzle equipped in a syringe pump and a high voltage of 24 kV was applied between a syringe needle and the drum collector, which were located 15 cm apart from each other. All processes were conducted at room temperature (~25 °C) under a controlled relative humidity of 30% and we could obtain the electrospun Me-PAN web from these processes [23]. The electrospun Me-PAN web was heated at a ramping rate of 1 °C min<sup>-1</sup> up to 280 °C, and then kept for 1 h under air as a stabilization step. Later, for the carbonization step to prepare the TM-CNFs, the stabilized Me-PAN web was carbonized at a ramping rate of 5 °C min<sup>-1</sup> up to 1000 °C for 1 h under N<sub>2</sub> environment. The prepared TM-CNFs were grinded with mortar for electrochemical experiments.

Ball-milling and water vapor activation were sequentially conducted as a carbon activation step with Co-CNFs in order to artificially change the pore structure. The ball-milling process was performed to uniformly control the size of Co-CNFs with zirconium oxide balls at a rotation speed of 500 rpm for 30 min [6]. The ratio of Co-CNFs and zirconium oxide balls is 1–50. After ball-milling process, the ball-milled Co-CNFs were heated up to 850 °C and activated for 1 h by supplying water at 60 °C to the quartz tube reactor with N<sub>2</sub> carrier gas at a flow rate of 200 ml min<sup>-1</sup> [24,25]. Moreover, removal of transition metal was also conducted to investigate the effect of remaining transition metal on ORR activity of TM-CNFs with nitric acid for 6 h at room temperature.

Electrochemical measurements were performed to evaluate the catalytic activity of the TM-CNFs by using a three electrodes cell connected to a potentiostat/galvanostat (Biologic, VSP). A smooth Pt wire was used as the counter electrode and Hg/HgO as the reference. All potentials that were initially measured versus (vs.) the Hg/HgO electrode immersed in 1 M NaOH were experimentally converted to a RHE scale by adding 0.94 V to the potentials [3,26]. We prepared the catalyst ink for coating the glassy carbon (GC) electrode by dispersing 10 mg synthesized catalysts in a mixture of 10 μl of 10 wt% Nafion solution (Sigma-Aldrich) and 2 ml solvent that is mixture of D.I. water and isopropyl alcohol with a ratio of 3–2. After the catalyst ink was sonicated for 30 min, 10 μl aliquot of the suspension was dropped onto GC electrode (0.2475 cm<sup>2</sup>) using a micropipette, so that the amount of the catalysts on the electrode is 200 μg cm<sup>-2</sup>. Cyclic voltammograms (CVs) were obtained at a scan rate of 10 mV s<sup>-1</sup> for a potential range from –1.2 V to 0.6 V (vs. Hg/HgO) at room temperature in 0.1 M KOH solution deaerated by bubbling ultrapure N<sub>2</sub>. Linear sweeping voltammetry (LSV) were also conducted at a rotating rate of 1600 rpm while oxygen was

constantly bubbled at a flow rate of 20 ml min<sup>-1</sup>; the potential was negatively scanned from 0.4 V to –0.8 V (vs. Hg/HgO) at a scan rate of 5 mV s<sup>-1</sup>.

Morphological properties of the catalysts were investigated thorough scanning transmission/transmission electron microscope (STEM/TEM; Philips TECNAI F20) located in Korea Basic Science Institute (KBSI), Gwangju center. In addition, The structural changes in the bulk crystallinity depending on the sorts of transition metal were analyzed using X-ray diffraction (XRD; Rigaku Miniflex II) equipped with Cu Kα (λ = 0.15406 nm). In order to determine the nitrogen content and composition on the surface of catalyst, the X-ray photoelectron spectroscopy (XPS) was measured on a VG MultiLab 2000 system (Thermo VG Scientific) in an ultrahigh vacuum (UHV) chamber with a base pressure ≤ 10<sup>-9</sup> Pa. All XPS spectra were obtained at room temperature using the Al Kα radiation (1486.6 eV) as X-ray source. The binding energy of the measured peaks is calibrated with respect to C 1s peak position (284.5 eV) and the standard Shirley background was used for the analysis. Moreover, the specific surface area and pore size distribution of TM-CNFs were also measured by N<sub>2</sub> adsorption using BET and BJH method, respectively at 77 K with an automatic gas adsorption-desorption apparatus (Belsorp-max, Japan).

## 3. Result and discussion

The TEM and STEM images of TM-CNFs show similar morphology regardless of different kind of metal and the most metal particles are homogeneously dispersed in CNFs whose diameter is approximately range around 300–500 nm (Figs. 1 and 2). The size of metal particles ranged around 10–50 nm and they are thoroughly covered with graphitic carbon structure [27]. However, for activated cobalt containing carbon nanofiber (A-Co-CNF), the morphology of carbon is slightly different with other TM-CNFs and the metal particles are agglomerated as shown in Figs. 1(d) and 2(d). It might be due to heat treatment at high temperature while water vapor that is usually used to activate the carbon materials is constantly supplied [24,25]. As a result, it is expected that the water vapor activation could improve ORR activity by increasing specific surface area due to formation of additional pore structure and increasing the amount of exposed metal particles that is considered one of the candidate for ORR active species.

On the other hand, there are remarkable differences in XRD patterns that are conducted to confirm the change of crystallinity of TM-CNFs (Fig. 3). Non-metal CNFs show a broad peak derived from the entangled turbostratic carbon structure of CNFs, whereas all TM-CNFs exhibit the development of the peak at 26°, which is attributable to the (0 0 2) plane of graphitic carbon (JCPDS card No. 75-2078). Furthermore, the final crystallinity of metal particles is totally different depending on kind of metal. In case of Co-CNF and Ni-CNF, the peak appears around 44°, 52°, and 76° which indicate the cubic structured cobalt (JCPDS card No. 15-0806) and nickel (JCPDS card No. 04-0850), respectively. In contrast, Fe-CNF shows a number of peaks and all could be indexed as orthorhombic structured iron carbide (Fe<sub>3</sub>C; JCPDS card No. 35-0772). These differences might be induced by different mechanism of applied metals in the catalytic graphitization. Among the inorganic and organic additives for catalytic graphitization, Fe usually combines with carbon to form carbides, while Co and Ni directly dissolve amorphous carbon in forming graphitic carbon process. Therefore, it is reasonably explained if we hypothesize that the Fe atoms are well bonded with the carbon to form Fe<sub>3</sub>C and the formation of Fe<sub>3</sub>C would lead to better dispersion and more pore structure formation [28].

In order to study the effect of transition metal on pore structure in carbon, the surface area and pore size distribution were measured using the N<sub>2</sub> adsorption isotherm.

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