Research paper

Comparative investigation of nitrogen species in transition metals incorporated carbon catalysts for the oxygen reduction reaction

Won Suk Jung[a], Yoongon Kim[a,b], Yuseong Noh[a], Hyunsu Han[a], Sungmin Park[a], Jinwoo Lee[a], Won Bae Kim[a,*]

[a] Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-ro, Nam-gu, Pohang 37673, South Korea
[b] School of Materials Science & Engineering, Gwangju Institute of Science and Technology (GIST), 261 Cheomdan-gwagiro, Buk-gu, Gwangju 500-712, South Korea

HIGHLIGHTS

- Non-PGM catalyst is prepared by en-TMs (Fe, Co, and Ni) complex and en only.
- Nitrogen is effectively doped as transition metals are atomically dispersed.
- The thickness of graphitic carbon shells for Fe@NC is thin.
- All catalysts show the consistent pyridinic-N concentration.
- The onset potential increases with the quaternary-N concentration.

ARTICLE INFO

ABSTRACT

The kinetic influences of transition metals (TMs) in non-platinum group metal (non-PGM) catalysts using ethylenediamine-TM (en-TM) complex are studied for the electro-reduction of oxygen. We exhibit that Ni atoms are inefficiently dispersed, which may influence the N doping as evidenced by XPS and elemental maps. High concentrations of N are attributed to the well-dispersed Co and Fe over the carbon. Electrochemical measurements demonstrate that the ORR on Co@NC and Fe@NC catalysts takes place faster than that on NC and Ni@NC catalysts. The correlation between the quaternary-N concentration of species and the onset potential with respect to TMs is investigated.

1. Introduction

Electrochemical ORR is one of the most important reactions in the energy conversion and storage since it is essential for fuel cells or metal-air batteries. Currently, sluggish kinetics is the primary issue in the ORR. Pt known as the best catalyst for the ORR is the scarce, costly, and electrochemically unstable, which results in significantly increasing efforts for the low Pt loading or replacement of the Pt catalyst [1–5]. Metal-oxides, polymers, 3-dimensional carbon nanosheets, carbon nanorods and carbon composite materials have been reported as the candidates to lower the Pt amount used or potentially to replace the Pt itself [6–13].

Carbon composite materials like TM-N-doped carbon catalysts have been intensively investigated since its kinetic parameters in literature are comparable or even almost equivalent to those of the Pt catalyst in the alkaline environment [14–16]. However, CO_2 in the feed gas stream can be transformed to carbonates in alkaline electrolytes, which results in a necessity of the utilization of pure H_2 and O_2 [17]. As well, low currents and complex water management may be necessary to be resolved [18]. Alkaline anion exchange membrane for the anion exchange membrane fuel cells (AEMFCs) needs to increase in mechanical stability and OH^- ion conductivity at elevated pH and temperatures in order to achieve comparable performance to proton exchange membrane fuel cells (PEMFCs).

Inversely, the poor kinetic parameters such as onset potential, Tafel slope, and half-wave potential of the TM-N-doped carbon composite catalysts are still challenged in the acidic environment as compared to the Pt catalyst. The high overpotential induced by sluggish kinetics causes the low open circuit potential for applications used in the real life. To resolve those issues, it is necessary to understand the relationship of materials and kinetic parameters in order to use the type of TM-N-doped carbon catalysts for the PEMFCs that can be more possible to
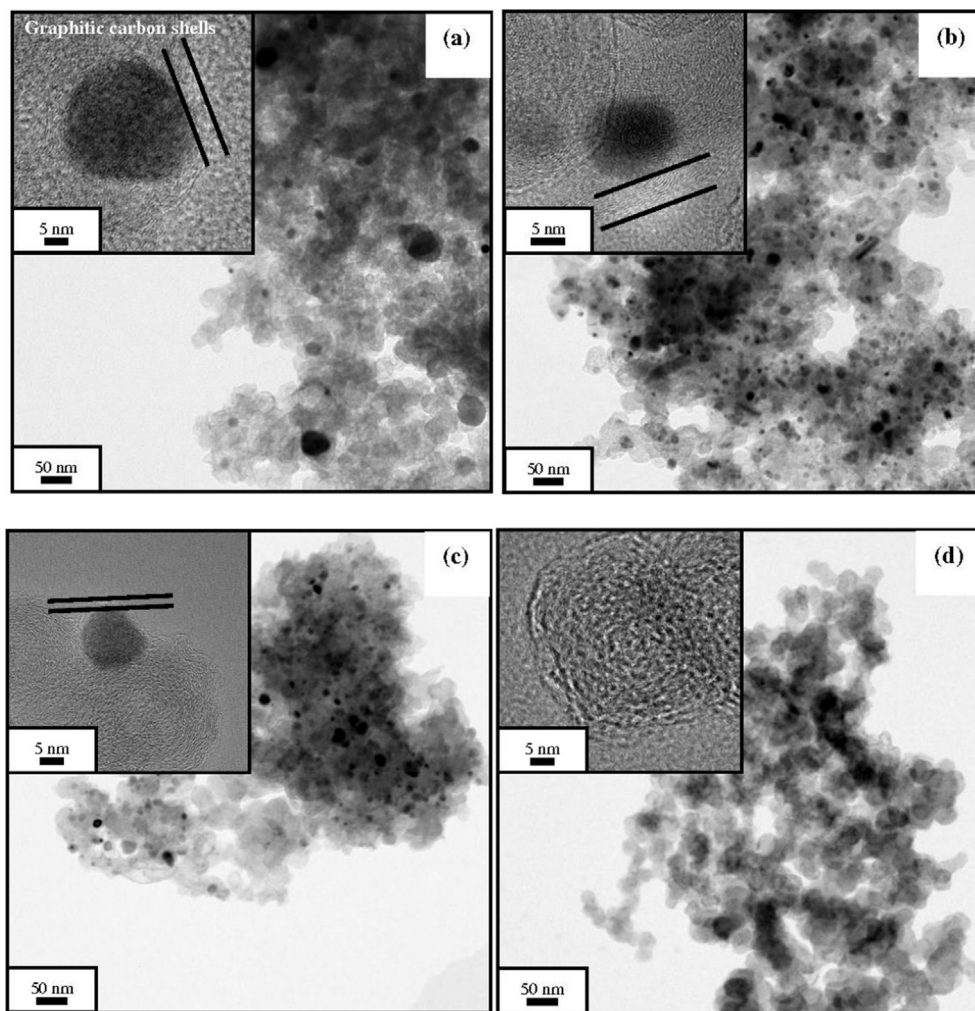

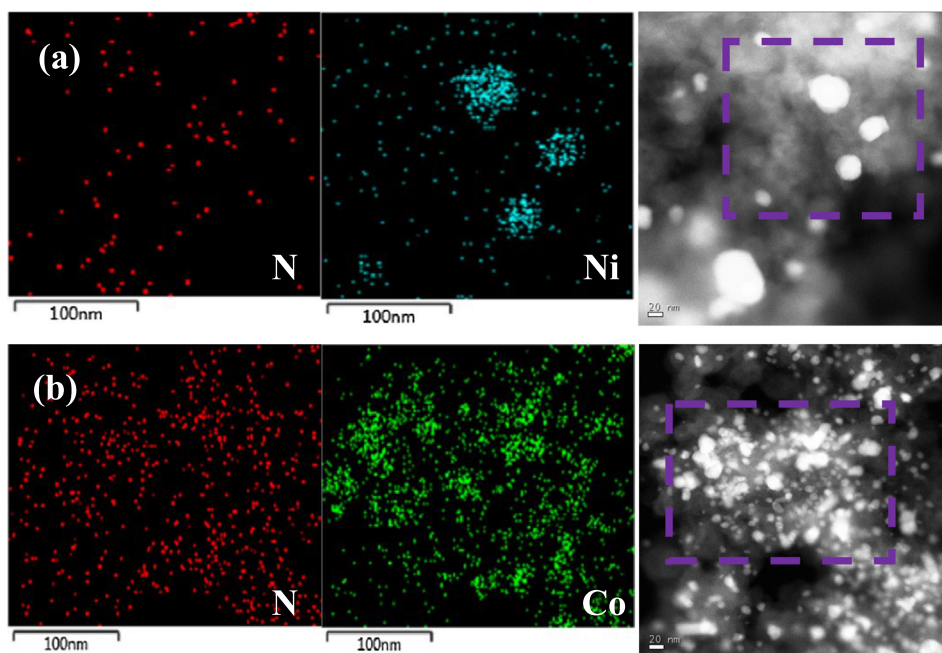**Fig. 1.** TEM images of (a) Ni@NC, (b) Co@NC, (c) Fe@NC, and (d) NC catalysts.

Fig. 2. HAADF-STEM images and EDS element mappings (TM and N) of (a) Ni@NC, (b) Co@NC, (c) Fe@NC, and (d) NC catalysts. (e) XRD patterns of Ni@NC, Co@NC, Fe@NC, NC and carbon black catalysts.