



A facile route for preparation of non-noble CNF cathode catalysts in alkaline ethanol fuel cells

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ABSTRACT

Non-precious metal incorporated carbon nanofiber (CNF) composite electrocatalysts for the oxygen reduction reaction (ORR) in alkaline media were developed via a facile approach, based on electrospinning and pyrolysis. According to successive material characterizations, most of the Fe and Co metals embedded in the carbon fibers (FeCo-CNF) were just used to facilitate the incorporation of nitrogen and oxygen species on the CNF surface more effectively without direct participating in the ORR. The experimental resultant FeCo-CNF catalysts were subsequently shown to possess the comparable electrocatalytic activity and the better tolerance to crossover ethanol than Pt/C in the ORR.

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1. Introduction

Of late, research into alkaline ethanol fuel cell systems has been increasing because of the increased potential application of platinum group metal (PGM)-free catalysts and low overpotential during cathodic reactions [1–4]. Although no dramatic breakthroughs have yet been made, various materials have been proposed as PGM-free catalysts for oxygen reduction reaction (ORR), an area in which great progress has been made, especially in the area of catalyst synthesis methods [5–15]. To this end, several research groups have reported their works on this preparation route, based on the use of various transition metals, nitrogen, and carbon containing species as precursors. For example, Dodelet et al. have used various approaches in the synthesis of non-precious metal catalysts for ORR, using NH_3 as a nitrogen source. The catalysts were fabricated via the wet impregnation of carbon black with an iron precursor, followed by a heat treatment in NH_3 coupled with various parameters [7–9]. In addition, Popov et al. recently developed a carbon-based metal-free catalyst with improved activity and selectivity

using organic nitrogen precursors [10,11]. Nitrogen-doped nanotubes/graphene and mesoporous graphitic arrays have been developed to enhance electrocatalytic activity, lower overpotential of the reaction, decrease crossover problem, and promote the stability, as compared to commercial Pt catalysts, especially in alkaline media [12–15].

Along with the chemical and electrochemical nature of the materials, the preparation method is another essential feature in the development of electrocatalysts as well as electrodes. Electrospun polymer fibers can be used as templates for the preparation of metal nanowire structure and/or for the better removal and recycling by strongly immobilized homogenous or heterogeneous catalysts in nanofibers [16–20]. Also, a large number of polymer/metal oxide composite fibers have been produced by electrospinning. In most of cases, the composite fibers could be converted into metal or metal oxide fibers by subsequent pyrolysis.

Herein, we report on our approach for preparing transition metal incorporated carbon nanofiber (CNF) cathode catalysts in order to enhance the electrocatalytic activity of ORR in alkaline media. The CNF structures obtained via electrospinning and subsequent pyrolysis have several advantages as fuel cell electrodes: (1) more contact points between the fibers lead to enhanced conductivity, (2) a web structure that enables a more homogenous heat transfer during high temperature treatments, and (3) cost-effectiveness due to the potential for mass production and the simplicity of the process.

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2. Experimental details

The electrospinning process was conducted using polyacrylonitrile (PAN), iron (III) acetylacetonate (Acc) and cobalt (II) acetylacetonate (Acc) dissolved in dimethylformamide (DMF), at concentrations of 10 wt% for PAN, 1.5 wt% for Fe(Acc)₃, and 1.5 wt% for Co(Acc)₂. After complete mixing of PAN in DMF solution, we dissolved two metal precursors into the 10 wt% PAN/DMF solution. A high voltage of 24 kV was then applied between a syringe and a collector. Here, the polymer solution was supplied at a flow rate of 3 ml h⁻¹ via a syringe pump. We also placed a rotating drum collector at a distance of 15 cm from the syringe end to collect the electrospun fibers. Note that all processes were performed at room temperature and below relative humidity of 30%.

Heat treatment was carried out at different temperatures and atmosphere, consecutively. The as-spun PAN nanofibers containing Fe and Co precursors were heated at a ramping rate of 1 °C min⁻¹ up to 280 °C, and then kept for 1 h in the air as a stabilization step. The stabilized fibers were subsequently heated for 1 h to 800 °C under N₂ atmosphere at a rate of 5 °C min⁻¹ to obtain Fe and Co containing carbonized nanofibers, *i.e.* FeCo-CNF.

Electrochemical measurements for evaluating the catalytic activity of the as-synthesized FeCo-CNF catalysts were performed by using a glassy carbon rotating disk electrode (RDE) attached to a potentiostat/galvanostat (Autolab, PGSTAT1287N). A platinized Pt wire and Hg/HgO were used as the counter and reference electrodes, respectively. Cyclic voltammograms (CVs) were subsequently obtained in a deaerated 0.1 M KOH at a scan rate of 50 mV s⁻¹ in a potential range of -0.9 to 0.5 V. Linear sweep voltammograms (LSVs) were measured in 0.1 M KOH at a scan rate of 5 mV s⁻¹ for a potential range of from 0.1 V to -0.9 V while oxygen was constantly bubbled. To observe a long-term stability, chronoamperometry (CA) was carried out by applying a constant potential of -0.2 V in 0.1 M KOH under O₂ saturation. To observe

the ethanol tolerance, we also measured the current voltage polarization in 0.1 M KOH + 0.5 M C₂H₅OH under O₂ saturation.

The surface morphology of the prepared electrode was analyzed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700) and transmission electron microscopy (TEM, JEOL JEM-2100). In addition, the crystal structure of the synthesized materials was investigated by X-ray diffraction (XRD, Rigaku Miniflex II), and the electronic state of the surface region was analyzed using X-ray photoelectron spectroscopy (XPS, VG Multilab 2000). Finally, the metal content was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 4300 DV).

3. Results and discussion

Fig. 1 shows the electrospun PAN nanofibers that were stabilized and consecutively carbonized. The introduction of a metal catalyst precursor promoted the formation of crystalline domains during carbonization of the nanofibers and the electrical conductivity of the carbon nanofibers is expected to increase with an increase of the metal content [21]. The high electrical conductivity of the carbon sheet containing Fe and Co particles and the structural advantage of the direct path from the one side to the other surface of the sheet makes this carbon electrode structure more favorable for use in the construction of fuel cell electrodes. The specific surface area of FeCo-CNF was 363 m² g⁻¹, 10% higher than that of metal-free CNF, but not remarkably higher than that of commercial carbon black (250 m² g⁻¹ for Vulcan XC). The diameters of the as-synthesized nanofibers range from 100 to 200 nm (Fig. 1(a)). Note that most of the metal particles are covered with graphitic layers of the carbon composite catalyst, with only a few partially on the surface despite the relatively high metal content of 22 wt% and a nanostructured whisker or fiber of graphitic carbon was formed as a result of the pyrolysis in the presence of Co and Fe (Figs. 1(b and c)) [15,22]. It is also clear that the nanoparticle size distribution is not uniform

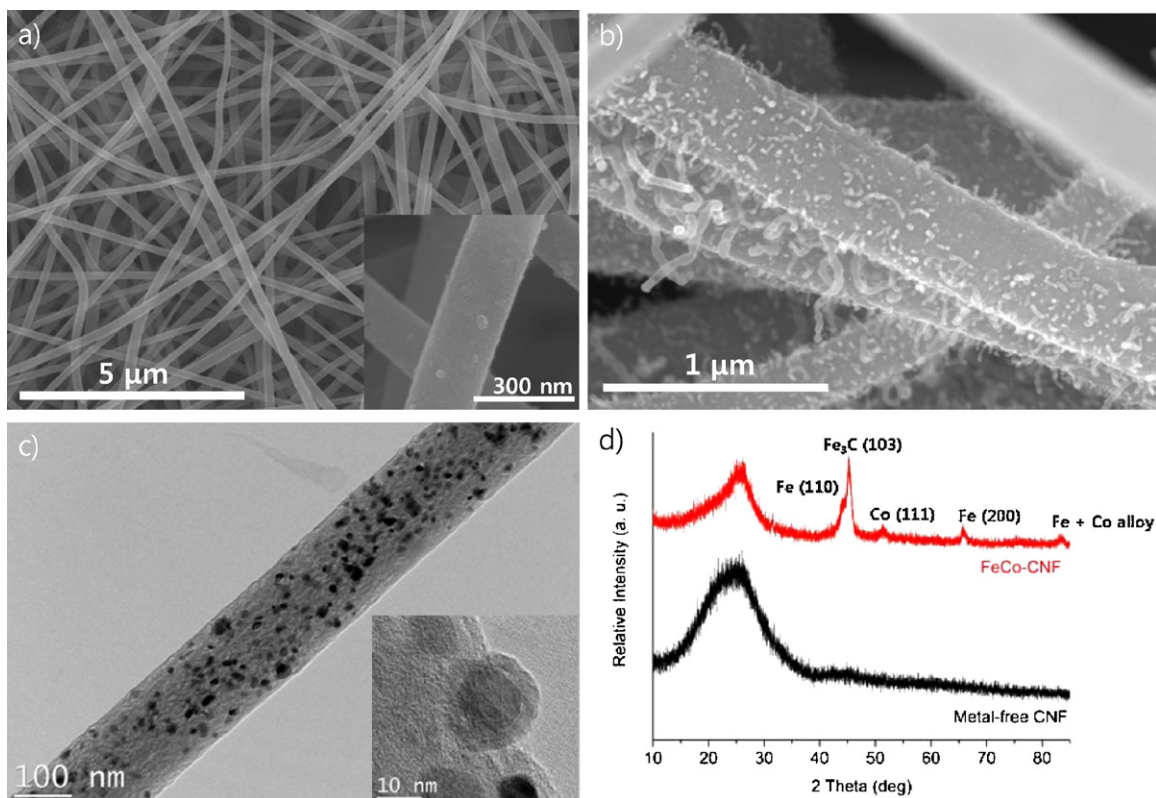


Fig. 1. (a and b) SEM and (c) TEM images of FeCo-CNF with magnified inset, respectively. (d) XRD patterns of FeCo-CNF and metal-free CNF, respectively.

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