Applied Catalysis B: Environmental 158–159 (2014) 355–360

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Nitrogen-doped carbon catalysts derived from ionic liquids in the presence of transition metals for the oxygen reduction reaction

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ARTICLE INFO

Article history:
Received 19 January 2014
Received in revised form 10 April 2014
Accepted 23 April 2014
Available online 2 May 2014

Keywords:
Non-precious catalyst
Nitrogen doped carbon
Ionic liquid
Oxygen reduction reaction
sp^2 Carbon network

ABSTRACT

Nitrogen-doped carbon catalysts for the oxygen reduction reaction (ORR) were synthesized by the pyrolysis of ionic liquids (IL), which are precursors of both nitrogen and carbon, using a silica hard template in the presence of a transition metal. From the linear sweep voltammogram recorded in an acidic solution, the ORR activity of the nitrogen-doped carbon catalysts increased significantly after the addition of the transition metal during the pyrolysis of the IL. From XPS-N 1s analysis, the introduction of the transition metal positively contributes to the formation of graphitic-N, which is known to be an active site for the ORR. The results of XPS-C 1s suggest a strong correlation between the sp^2-carbon network and the ORR activity. Co is a more effective metal compared to Ni due to the creation of a higher degree of sp^2-carbon networks for fast electron transfer during the ORR. Based on the quantitative analysis of the experimental results, the IL is a promising precursor for nitrogen-doped carbon catalysts, and the addition of a transition metal is essential for improved activity of the ORR.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been recognized as potential electricity generating devices with a low environmental impact and high efficiency especially for application as automotive and stationary power sources [1–3]. Because PEMFCs are a type of electrochemical device, electrocatalysts play important roles in determining the performances of PEMFCs. Conventionally, Pt-based catalysts are commonly used as catalysts on both the cathode and the anode. Because the rate of the oxygen reduction reaction (ORR) occurring at the cathode is much slower than the rate of the hydrogen oxidation reaction at anode, the cathode requires much larger quantities of precious catalysts [4]. Therefore, a high cost and a limited supply of Pt have prevented the successful commercialization of PEMFCs.

Among the various alternatives for Pt-based catalysts [5–10], carbon-based materials, especially nitrogen-doped carbon, are of great interest as non-precious metal catalysts for the ORR due to their relatively high activity and superior stability [11–16]. Li et al. demonstrated that the presence of nitrogen on the carbon nanotube (CNT) induces a high ORR activity that is comparable to Pt based catalysts in an alkaline medium [17]. The multi-walled N-doped CNT containing 8.4 at.% nitrogen exhibited a high ORR catalytic activity as well as an improved stability due to the durable physical characteristics of the CNTs. In an effort to enhance the catalytic activity of nitrogen-doped carbon, transition metals were introduced to nitrogen containing complexes [18–21]. The transition metal itself does not participate in the ORR but serves to catalyze the formation of nitrogen-doping structures in the carbon framework that are active toward the ORR [13,22,23]. Therefore, the nitrogen content and doping structure in the carbon materials are expected to be a governing factor for the ORR activity.

In this regard, several attempts have been made to increase the nitrogen content in carbon based materials by employing precursors with a high nitrogen content, such as ionic liquids (ILs) [24–27]. A variety of ionic liquids were investigated as precursors for the preparation of nitrogen-doped carbon [28], and additives were incorporated as a nitrogen donor to increase the nitrogen content of the material [29]. However, relatively little work has been dedicated to investigating the effect of transition metals on the formation of nitrogen functional groups when IL are used as precursors and the activity of these catalysts for the ORR, especially in acidic media.

Therefore, we experimentally examined the ORR activity of nitrogen-doped carbon materials prepared by pyrolysis of ionic liquids (i.e., 1-ethyl-3-methylimidazolium dicyanamide ($C_8H_{11}N_5$,

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http://dx.doi.org/10.1016/j.apcatb.2014.04.038

Emim-dca) as a nitrogen and carbon precursor) in the presence of various transition metals. Based on the results, the effect of the transition metal on the activity of the ORR was investigated, and the enhanced ORR activity was correlated with the nitrogen-doped structure and sp^2 degree of carbon network in the nitrogen-doped carbon catalysts.

2. Experimental

2.1. Catalyst synthesis

The nitrogen-doped carbon-based catalysts investigated in this paper were synthesized by the pyrolysis of a mixture consisting of an ionic liquid, silica suspension, and transition metal salts. In detail, an ionic liquid (i.e.,1-ethyl-3-methylimidazolium dicyanamide ($C_8H_{11}N_5$, Emim-dca)), which is composed of only C, H, and N, acts as a nitrogen and carbon precursor, and silica suspension and transition metal salts are employed as hard template and nitrogen-doping aide, respectively. Initially, different amounts of a cobalt salt ($Co(NO_3)_2{\cdot}6H_2O$) were dissolved in de-ionized water to prepare catalysts containing different Co loadings (i.e., 5, 10, 15 wt.%). This ratio indicates the proportion of cobalt to the carbon carbonized from the ionic liquid. Next, Emim-dca (1 g, from BASF) and a silica suspension (2.5 g, LUDOX HS40) were added to the dissolved Co solution followed by ultra-sonication to uniformly disperse the silica template in the solution. The resulting homogeneous mixture was pyrolyzed under argon in two steps. First, the mixture was pyrolyzed for 1 h at 300 °C to completely remove the water, and then, the mixture was pyrolyzed for an additional 1 h at 800 °C to carbonize the sample. After the pyrolysis, the black power was treated with a HF solution for 3 h to leach out the excess metal elements and etch the silica templates, which was thoroughly washing several times with de-ionized water. The catalyst was dried in a vacuum oven at 80 °C overnight, and each resulting catalyst was denoted IL + Si + CoM, where M indicates the metal content (wt.%) of the sample. For comparison, IL, IL + Co10 and IL + Si were also synthesized by the procedure mentioned above except that the silica suspension and cobalt nitrate, respectively. Nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) was also applied as a transition metal salt instead of cobalt nitrate to determine the effect of different transition metal. The sample with different transition metal, Ni, was synthesized with 10 wt.% of transition metal and denoted as IL + Si + Ni10.

2.2. Electrochemical characterization

The electrochemical properties of the prepared nitrogen-doped carbon-based catalysts were analyzed using a rotating ring-disk electrode (RRDE, Pine Research Instruments). The experiments were conducted using a conventional three-electrode system equipped with a platinum wire counter electrode and a Hg/Hg_2SO_4 reference electrode in a 0.5 M H_2SO_4 electrolyte. For the working electrode, the prepared catalyst was coated onto a glassy carbon electrode as a thin film. The catalyst ink was prepared by the method described in our previous study on N-doped carbon [30]. 8 mg of the catalyst powder was ultrasonically dispersed in a solution containing 0.5 mL of isopropyl alcohol (IPA), 1.5 mL of de-ionized water and 50 μL of 5 wt.% Nafion solution. Then, the catalyst ink (15 μL) was dropped onto the glassy carbon disk of the RRDE, which was followed by drying in a nitrogen atmosphere at room temperature. Linear-sweep voltammograms were recorded in the potential range between 1.0 and 0.0 V_{SHE} at a scan rate of 5 $mV\,s^{-1}$ and a rotating speed of 1200 rpm.

Table 1
BET and ICP analysis of the prepared catalysts. ICP was obtained before and after acidic leaching in a HF solution for 3 h.

	Specific surface area ($m^2\,g^{-1}$)	Co content (wt.%)	
		Before leaching	After leaching
IL	3.41	–	–
IL + Si	1309	–	–
IL + Si + Co5	975	4.2	3.2
IL + Si + Co10	824	8.3	2.6
IL + Si + Co15	645	13.2	2.2

2.3. Physical characterization

High-resolution transmission electron microscopy (HR-TEM, JEM-30100 model) was performed to observe the morphology of the carbon structure. Photoelectron spectroscopy (XPS, K-alpha, Thermo, UK) was performed to analyze the surface composition of the catalysts. The nitrogen content in the bulk samples was measured using an elemental analyzer (EA, 2400 Series II CHNS/O Analyzer, PerkinElmer Co., USA). The transition metal loading that remained in each catalyst was estimated using an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. Brunauer–Emmett–Teller (BET) nitrogen adsorption isotherms were recorded using on a Micromeritics TriStar analyzer at 77 K.

3. Results and discussion

HR-TEM analysis was performed to characterize the morphologies of the nitrogen-doped carbons prepared by the pyrolysis of the IL using the silica template (IL + Si) and the addition of a transition metal (IL + Si + Co10). As shown in Fig. 1a, the nitrogen-doped carbon synthesized by pyrolysis of the IL without any additives resulted in a thin carbon sheet without pores. However, the morphology of the catalyst changed after the introduction of 12 nm silica nanoparticles (LUDOX-HS40), which were used as a hard template, as shown in Fig. 1b. It can be clearly observed that the removal of silica particles using the acidic etching process creates a highly porous structure in the nitrogen-doped carbon. The specific surface area determined by BET analysis significantly increases from 3.41 $m^2\,g^{-1}$ to 1309 $m^2\,g^{-1}$ after application of the silica template. Because the HR-TEM images of Fig. 1b and c are quite similar, the addition of Co to the IL + Si catalyst does not drastically change the porous structure. However, the specific surface area decreases linearly to 645 $m^2\,g^{-1}$ as the amount of added cobalt increases from 0 wt.% to 15 wt.%. According to the ICP measurement used to quantify the Co content before and after the chemical leaching process, the initial Co content was close to the nominal target, as shown in Table 1. In contrast, after chemical leaching, the residual Co content appears to be nearly same between 2.2 and 3.2 wt.% regardless of the initial Co content. The metallic Co that survived the severe chemical leaching process is primarily due to the formation of a barrier, such as encapsulation of the carbon layers during the pyrolysis process [22,31]. Therefore, the reduced specific surface area upon addition of Co is not associated with the residual Co content.

The ORR catalytic activities for the nitrogen-doped carbon catalysts synthesized from IL were evaluated by linear sweep voltammetry using a rotating ring disk electrode system in a 0.5 M O_2-saturated H_2SO_4 solution. As shown in Fig. 2, the lowest ORR activity was observed for the catalyst prepared by the pyrolysis of the IL only. After application of the silica nanoparticles as a hard template, the ORR catalytic activity improved due to the increased surface area, which was determined from the BET results. It is important to note that a dramatic improvement in the activity was observed with the simultaneous addition of the silica template and Co. The ORR activity increases with addition of Co up to 10 wt.%