Fuel 102 (2012) 359–365

Contents lists available at SciVerse ScienceDirect

Fuel

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

Iron addition to Vietnam anthracite coal and its nitrogen doping as a PEFC non-platinum cathode catalyst

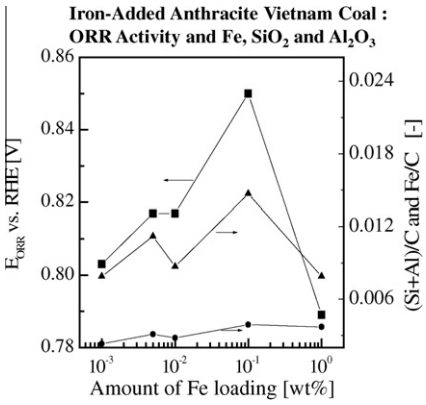
Mitsuyoshi Muraoka, Hiroyuki Tominaga, Masatoshi Nagai *

Graduate School of Bio-applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24 Nakamachi, Koganei, Tokyo 184-8588, Japan

HIGHLIGHTS

- Iron addition to Vietnam anthracite coal as a PEFC non-platinum cathode catalyst.
- Nitrogen doping without iron addition promoted no ORR activity of the Vietnam coal.
- Iron addition from 10 ppm to 0.1 wt% significantly increased ORR activity.
- Nitrogen doping at 1073 K and iron addition significantly increased the micropore area.
- The ORR potential was related to the iron, nitrogen species and SiO_2 and Al_2O_3.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 April 2011
Received in revised form 16 May 2012
Accepted 17 May 2012
Available online 29 May 2012

Keywords:
Iron addition
Nitrogen doping
Non-precious metal catalyst
PEFC
Vietnam anthracite coal

ABSTRACT

The iron addition to Vietnam anthracite coal, subsequent nitrogen doping at 1073 K and its catalyst activity for the oxygen reduction reaction (ORR) were studied for application as an alternative platinum catalyst in a polymer electrolyte fuel cell. The ORR activity of the coal catalyst was determined by a three–electrode electrochemical measurement. The nitrogen doping without iron addition promoted hardly any activity of the Vietnam coal for the ORR, but the iron addition from 0.001 to 0.1 wt% caused a significant increase. The addition of 0.1 wt% iron to the Vietnam coal provided the highest ORR at 0.85 V vs. RHE at -0.005 mA/cm^2. However, the addition of 1.0 wt% iron formed several iron particles of 10–30 nm based on transmission electron microscopy measurement and decreased the ORR activity. From the X-ray photoelectron spectroscopy analysis of the non-added and iron-added Vietnam coals, the N/C, Fe/C and (Si + Al)/C ratios exhibited a maximum peak at the 0.005 wt% iron-added level, while the two latter ratios exhibited another high peak at 0.1 wt%. The nitrogen doping of Vietnam coal at 1073 K significantly increased from 5 to 1050 m^2/g surface area with 96% slit–shaped micropores and generated nitrogen species having a disordered structure. The ORR activity of the treated Vietnam coal was related to the iron, nitrogen species and the ash components, such as Si and Al. The active structure of the iron added coal-derived electrocatalysts was discussed.

1. Introduction

Non-platinum catalysts are being significantly developed for a polymer electrolyte fuel cell (PEFC) to be used in automotive and stationary applications. The major challenges in fuel cell research are to reduce the cost of the electrocatalyst either by decreasing the Pt loading or by developing non-noble catalysts. Coal consists of carbon, hydrogen and oxygen elements, and also contains nitrogen, iron and other metals as impurities. Anthracite of the various coals, possesses a high carbon percentage, low oxygen and fewer minerals than the other low rank coals with a high graphite

* Corresponding author. Tel./fax: +81 42 388 7060.
E-mail address: mnagai@cc.tuat.ac.jp (M. Nagai).

0016-2361/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2012.05.029

structure [1,2] and electrochemical performance [3–5]. Anthracite was selected as an alternative platinum cathode catalyst in this study. In a previous paper [6], the Vietnam anthracite coal nitrogen-doped with NH_3 exhibited very poor activity for the oxygen reduction reaction (ORR), although the other low rank coals, such as brown and bituminous coals promoted the ORR. The nitrogen doping of carbons without any metals is reported to show a lower activity for the ORR of a PEFC [7–10], suggesting that the pyridinic and quaternary nitrogens acted as active sites of the non-metal free catalyst for the ORR. The pyrolysis or nitrogen doping of iron or cobalt compounds to graphite showed a good performance as a non-platinum catalyst [11–14]. Iron particles grew on the carbon nanostructures with a high percentage at the exposed edge plane. However, the active species of the catalyst using the nitrogen-doped carbons with iron for the ORR are not fully understood. Therefore, the effect of the iron addition to the Vietnam anthracite coal on the catalyst properties and ORR onset potential activity was determined. The active species of the coal were studied on the basis of the N_2 adsorption, transmission electron microscope (TEM) measurements, XRD, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The promotion by the iron addition and the ash elements of SiO_2 and Al_2O_3 was also discussed.

2. Experimental

Vietnam coal is used as the representative anthracite coal. Its compositions in the JCOAL supply are shown in Table 1. The coal (3.0 g) was crushed and ground in 20 ml of ethanol using a planet–wheel agate ball mill consisting of a 250 ml container with 15 agate balls (Freche Co.) at 300 rpm for 0.5 h. The coal was ground and left in a dryer at 353 K for 12 h. The ground coal (0.15 g) was packed in a microreactor and raised to the desired temperature (1073 K) at a rate of 2 K/min in a stream of 60 ml NH_3 and maintained at this temperature for 3 h. After nitrogen doping, the ammonia was switched to helium and cooled to room temperature. The addition of iron to the coal was determined using an aqueous solution of $FeCl_3{\cdot}6H_2O$, after the coal was washed with a 5 M HCl solution, the iron was added and subsequently nitrogen-doped in a stream of NH_3. The N_2 physical adsorption experiment with the catalyst was performed using an Omnisorp 100CX volumetric analyzer (Beckman Coulter Co.) at 77 K after drying under vacuum at 473 K for 2 h. The mesopore and macropore areas of the coal were determined by a *t*-plot analysis. The surface morphology of the catalysts was determined by a TEM analysis using a JEM-2100F transmission electron microscope (Japan Electronic Corp.). The XRD patterns of the coals were determined using a RINT-2100VPC/N (Rigaku Co.) with Cu Kα radiation. The Raman analysis was carried out using a Nicolet Almega XR spectrometer at the laser beam of 352 nm. Ten data points were taken at each position, and then deconvoluted: 1610–1620 cm^{-1} for D_2, ca 1590 cm^{-1} for G band, for D_1, 1530–1540 cm^{-1} for D_3, ca 1350 cm^{-1} for D_1 and ca 1180 cm^{-1} for D_4. The defect degrees of the graphite were calculated using average data based on the areal ratio (A_{D1}/A_G) of the D_1 band at ca. 1350 cm^{-1} to the G band at ca 1590 cm^{-1} [15–17]. The XPS analysis was carried out using an ESCA 320 (Shimadzu Co.) at 240 W. The XPS spectra C 1s and O 2p were determined by etching with argon for one min in the ranges of 282.5–292.0 and 523.0–543.0 eV, respectively, by the Shirley baseline correction. The binding energies of the N_{1s} and Fe 3d spectra were determined at 395.0–425.0 and 700.0–735.0 eV, respectively, by the linear correction, and those of Al 2p and Si 2p were determined at 63.0–83.0 and 89.2–109.2 eV, respectively, by the Shirley baseline correction. The peaks were corrected at the C 1s peak of 284.6 eV.

The voltammetric measurement was performed using a ring rotating disk electrode (RRDE) composed of a carbon stick as the anode, a glassy-carbon ring disk as the working electrode at 2000 rpm, and a standard Ag/AgCl as the reference electrode which was labeled on a real hydrogen electrode (RHE, + 0.199 V vs. RHE). The catalyst (0.028 mg) was dispersed in a 0.02 mL suspension of a 35% aqueous solution of ethanol and then sonicated to form 0.142 mg/cm^2 based on the geometric area (disk area, 0.196 cm^2 and ring disk electrode, 0.071 cm^2). After the application, a 5-μL aliquot of a 2-propanol solution containing a 0.05 wt% Nafion (Aldrich) was dropped onto the glassy-carbon disk. The RRDE attached to a three-compartment electrochemical cell was placed in a 0.5 M H_2SO_4 solution. The potential was controlled using a potentiostat. The measurement was carried out at room temperature and a rotation speed of 2000 rpm at 50 mV/s for the cyclic voltammetry (CV) and at 5 mV/s with scans between 0.05 and 1.00 V vs. RHE for the linear sweep voltammetry (LSV) with scans from 1.00 to 0.05 V to determine the current density in Ar and O_2 (21.8 ml/min). The scanning was carried out several times to obtain the steady state values. The current density was obtained with the current normalized to the disk geometric area and estimated at 0.6 V vs. RHE. To evaluate the ORR activity, the steady state of the LSV was measured from the difference between the voltammograms obtained in the Ar and O_2 atmospheres. The onset potential for the ORR was measured at −0.005 mA/disk cm^2.

3. Results and discussion

3.1. Surface morphology of the nitrogen-doped coal

The isotherms of Vietnam coal before (a) and after (b) the nitrogen doping are shown in Fig. 1. Both isotherms exhibited chars at the low relative pressure of a I type monolayer adsorption, showing a slit-shaped structure. The adsorptions of N_2 on the raw and treated Vietnam coals were very small at a high relative pressure. The micropores of the nitrogen-doped coals distributed at 85–96%, showed tremendously small macropores in the ranges of the flat curve at the P/P_0 of around 0–0.95. The BET surface area of the coal is shown in Table 2. Although the surface area of the raw Vietnam coal was 5 m^2/g, the nitrogen doping of the Vietnam coal in flowing

Table 1
Elemental and proximate analyses of raw and nitrogen doping Vietnam coal at 1073 K.

	Elemental analysis (wt%)					Proximate analysis (wt%)		
	C	H	N	O	Ash	Fixed carbon	Volatile matter	Moisture
Raw coal[a]	89.2	3.2	1.0	1.5	4.6[b,c]	87.6	6.4	1.4
1073 K-nitrided coal[d]	91.8	0.70	2.1	2.8	2.6[c]	96.9	0.5[e]	0.0

[a] Database of JCOAL (Japan coal energy center).
[b] Ash (JCOAL analysis data): SiO_2, 46.3; Al_2O_3, 34.9; Fe_2O_3, 8.89; CaO, 1.71; MgO, 1.22; K_2O, 3.38; SO_3, 1.12; TiO_2, 0.88; Na_2O, 0.51; P_2O_5, 0.39; MnO, 0.06; V_2O_5, 0.05 wt%.
[c] Iron content (Fe/C) of the raw and nitrogen doping Vietnam coal at 1073 K by XPS analysis: 0.0016 and 0.0013, respectively. Fe content of raw Vietnam coal and Fe-removed raw coal were 0.41 and 0.002 wt%, respectively, using ICP.
[d] Measured by Analysis Center of Nihon University (elemental analysis of raw coal: C, 86.7; H, 3.0; N, 1.3; O, 6.3; Ash, 2.7).
[e] Calculated by TG analysis (subtraction from the weight at 1198 K from the weight 1073 K).