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Coals as a novel cathode catalyst for polymer electrolyte fuel cell

Mitsuyoshi Muraoka, Masatoshi Nagai *

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

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ABSTRACT

Coal has been developed as a new non-noble metal cathode catalyst for a polymer electrolyte fuel cell. The activities of four ranks of coals (anthracite, bituminous, sub-bituminous and brown coals) for the oxygen reduction reaction (ORR) were determined based on heat treatment in streams of various gases, nitridation and the iron addition effect. The surface area depended on the micropores of the nitrided coals distributed at 85–96%, thus showing extremely higher internal microporous surface areas. The XRD measurement suggested that the tested coals had a domain assembly composed of microdomains of approximately three layers of graphene with an interlayer distance of 0.37 nm and a layer length of 1.15 nm. The high-power decoupling CP/MAS ^{13}C NMR analysis of the nitrided Adaro coal showed the presence of little hydrogen in the fringe of the fused aromatic compounds of the nitrided coal. The treatment of the coals in a stream of NH_3 exhibited a higher ORR potential vs. RHE than those in the nitrogen and 20% CH_4/H_2 streams. The 1073 K-nitrided brown and sub-bituminous coals were significantly active for the ORR, while the nitrided anthracite coal was less active. Based on the XPS analysis, the introduction of nitrogen atoms formed a deficit structure with the pyridinic nitrogen.

1. Introduction

A polymer electrolyte fuel cell (PEFC) is very effective for reducing CO_2 emissions and exhaust gases from automobiles into the atmosphere. The platinum loaded on the catalyst is quite expensive and in short supply. As a result, reduction of the Pt amount in a PEFC is a key issue for popularization of the PEFC. Coal is very cheap and inexhaustible deposits exist all over the world. Coal possesses a graphene and stacking structure [1,2] which mainly consists of carbon, hydrogen and oxygen elements. The geologically available amounts of coal are vast, but its composition strongly depends on its carbonization degree, occurrence and deposition age. These factors govern the characteristics and reactivity of coal which is classified as anthracite, bituminous, sub-bituminous and brown coals. Their elements, especially nitrogen and iron, would induce the catalytic activity for the oxygen reduction reaction (ORR) [3,4]. Recently, bituminous coal- and coal tar-derived carbons have been studied for use as electrode materials in supercapacitors [5,6] and the negative electrode of lithium-iron batteries using graphite materials [7]. Moreover, nitrogen-doped carbons, such as graphite [8,9], nanotube [10,11] and graphene [12,13] have been extensively studied and have demonstrated high electrocatalytic activity for the oxygen reduction reaction (ORR). As coal is heated with several gases, the carbon structure and micropores of the treated coal are expected to change due to the release of volatile matter. Consequently, the nitrogen-doped coals are available as an alternative Pt catalyst for a fuel cell. However, little or no or little attention has been given to the application of coal as the catalyst in a PEFC. In this study, we focused on the utilization of the coals from Vietnam (anthracite), Wandoan and Illinois No. 6 (bituminous), Adaro (sub-bituminous), and Australia A and B (brown) as a cathode catalyst. The effects of the treatment of the coals with various gases and washing with an aqueous HCl solution to remove any incorporated metals on the ORR potential and current density of the cathode were determined. Although raw coal was not active in electrical reactions, the coal heated in a stream of ammonia out of several gases turned out to be active in the ORR and was available as a fuel catalyst. The changes in the surface structure, composition and morphology of the coals by nitridation in a stream of NH_3 were studied by N_2 adsorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), carbon-13 nuclear magnetic resonance (^{13}C NMR), and X-ray photoelectron spectroscopy (XPS). The generation of the active species of the coal-derived electrocatalysts for a highly active ORR activity was examined.

2. Experimental

Vietnam (anthracite), Wandoan and Illinois No. 6 (bituminous), Adaro (sub-bituminous) and Australia A (JCOAL, SS002) and B (JCOAL, SS052) (brown) coals were used as the representative coals. Their compositions are shown in Table 1. The coals (3.0 g) were

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

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Table 1
Elemental analysis of the various raw coals.

Coal	Elemental analysis (wt%) (d.a.f.)				
	C	H	N	O	Ash[a]
Vietnam	86.7	3.0	1.3	6.3	2.7
Wandoan	64.2	5.2	0.9	19.8	9.9
Illinois No. 6	57.7	4.1	1.2	18.1	14.7
Adaro	64.3	4.9	1.3	24.5	5.0
Australia A	66.4	5.1	1.4	9.9	17.2
Australia B	73.0	4.9	2.0	8.9	10.5

[a] Fe content (Fe/C) of raw and 1073 k-nitrided coals by XPS analysis: Vietnam, 0.0016 and 0.0013; Australia A, 0.002 and 0.004; Adaro, respectively.

crushed and ground in 20 ml of ethanol using a planet-wheel agate ball mill (Freche Co.) at 300 rpm for 0.5 h. The ground coal was then stored in a dryer at 353 K for about 12 h. The ground coals (0.15 g) without HCl-treatment were packed in a microreactor and raised to a final temperature (673–1073 K) at the ramping rate of 2 K/min and in a stream of 60 ml/min of NH_3 (N_2 or 20% CH_4/H_2). After the coal sample was maintained at the final temperature for 3 h, the NH_3 was switched to He and the catalyst was cooled to room temperature. Demineralized coals were prepared by successive washing with a 5 M HCl aqueous solution at room temperature using a mixer. The iron addition to the HCl-washed coal by an aqueous solution of $FeCl_3$, followed by nitriding in a stream of NH_3, was studied for its effect on the cathode activity.

The N_2 physical adsorption experiment with the catalysts 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 macropore surface area of the coal was determined by a t-plot analysis, and the micropore area was calculated by the difference between the total and macropore areas. 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 solid state ^{13}C NMR analysis of Adaro coal was carried out using an ECX-400 (Japan Electronic Co.) by the cross polarization/magic angle spinning (CP/MAS) and high-power decoupling method. The XPS analysis was carried out using an ESCA 320 (Shimadzu Co.) at a power of 240 W. The XPS spectra of the O 2p, Al 2p and K 2p regions were determined by etching with argon for one min. in the ranges of 523.0–543.0 eV, 63.0–83.0 eV and 283.0–303.0 eV, respectively. The N 1s binding energies were deconvoluted to three nitrogen types (pyrrole-N, 400.5; pyridine-N, 398.6; quaternary-N, 401.6 and N-oxide, 403.1 eV) [14,15]. The peak shift correction was based on the C1s at 284.6 eV.

The voltammetric measurement was performed using a ring rotating disk electrode (RRDE) (Nikkou Keisoku Co.) composed of a carbon rod as the anode, a standard Ag/AgCl reference, a glassy-carbon ring disk as the working electrode, and a potentiostat. The catalyst (28 μg) was dispersed in a 20 μl suspension of a 35 vol% aqueous solution of ethanol to form a 1.4 cat-mg/ml solution. After 14 μg of the catalyst was applied to the disk (71.4 μg/cm^2 based on the geometric area (0.196 cm^2)), the RRDE attached to a three-compartment electrochemical cell was placed in the 0.5 M H_2SO_4 electrolyte. The measurement was carried out at room temperature and a rotation speed of 2000 rpm at 50 mV/s for cyclic voltammetry (CV) and at 5 mV/s with scans between 0.05 and 1.00 V vs. RHE for 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 steady state values. To evaluate the ORR activity, a steady state LSV was measured from the difference between the voltammograms obtained in the Ar and O_2 atmospheres.

3. Results and discussion

3.1. Nitridation

Fig. 1A shows the H/C and O/C ratios of the coals before and after nitridation based on the elemental analysis. The nitridation of all the coals significantly decreased by one order of magnitude the H/C ratio (from 0.8–0.95 to 0.09–0.2) and decreased the O/C ratio by 0.25–0.5 times (from 0.05–0.28 to 0.02–0.12). The raw Vietnam coal had a low H/C ratio (0.4) and low O/C ratio (0.05), and nitridation greatly decreased the H/C ratio to 0.10 and the O/C ratio to 0.025. However, carbonization decreased the H/C ratio to 0.43 and O/C to 0.024, indicating similar decreasing ratio of the O/C but little change in the H/C ratio. These results indicated that the NH_3 nitridation eliminated especially the hydrogen atom and generated new carbon species. An increase in the nitrogen contents of the various coals was observed after nitridation at 1073 K (Fig. 1B). The nitridation of the Wandoan and Australia A coals inversely increased the nitrogen contents from 1.4% to 2.9% and from 0.7% to 4.3%, respectively. Thus, doping nitrogen in the coal depended on the low carbonization of the coal; i.e., the oxygen atoms of the brown coals were easily lost or the oxygens exchanged with the nitrogens. The brown coals were more active for the ORR after nitridation, while the nitridation of the anthracite coal was slowed because of the highly carbonized coal and low oxygen content. The nitridation of the ground brown coal (0.15 g) at 1073 K caused a loss of approximately 0.05 g of the nitrided coal (70% weight loss). Consequently, the ORR activity of the nitrided coals was related to the decreasing oxygen and hydrogen contents as well as the increasing nitrogen of the coal like nitrided graphite.

3.2. BET surface area and TEM image of Adaro coal

The isotherms of Adaro coal before and after nitridation are shown in Fig. 2. The adsorption isotherms showed a I type

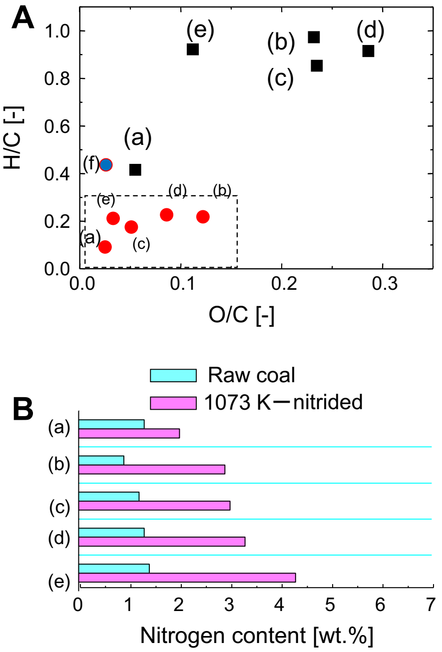

Fig. 1. (A) H/C ratio plotted vs. O/C ratio of Adaro coal (■) before and (●) after nitridation of (a) Vietnam, (b) Wandoan, (c) Illinois No. 6, (d) Adaro and (e) Australia A coals at 1073 K. (f) ● The ratios of H/C and O/C of carbonization of Vietnam coal at 1073 K. (B) Nitrogen contents (upper column) before and (lower column) after the nitridation at 1073 K.