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Examination of the electroactive composites containing cobalt nanoclusters and nitrogen-doped nanostructured carbon as electrocatalysts for oxygen reduction reaction

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HIGHLIGHTS

- ► The electroactive composites are prepared by a simple and inexpensive method.
- ► Synthesis temperature affects metallic Co size, level of N-doping and graphitization.
- ► The electrocatalysts are active in oxygen reduction reaction in alkaline solution.

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ABSTRACT

A series of electroactive composites containing cobalt nanoclusters and N-doped graphite-like carbon is obtained by catalytic chemical vapour deposition (CCVD) using Mg–Co–Al layered double hydroxides and acetonitrile. The influence of synthesis temperature, e.g. 600, 700 and 800 °C on their physico-chemical properties is examined by means of X-ray diffraction, elemental analysis, thermal analysis, nitrogen sorption, Raman spectroscopy, X-ray photoelectron spectroscopy, scanning and transmission electron microscopy.

N-doped graphite-like carbon in the catalysts shows various morphologies. The composite prepared at 600 °C contains plate-like particles, whereas those synthesized at 700 and 800 °C, contain not only plate-like particles but also multi-walled carbon nanotubes. The concentration of nitrogen uniformly incorporated in the carbon framework is ca. 2 wt %.

The electrocatalytic properties of the catalysts for oxygen reduction reaction (ORR) are evaluated in alkaline media by cyclic voltammetry and rotating disk electrode (RDE) measurement. The composites are proved to have the ability to reduce oxygen according to 2-electron pathway.

1. Introduction

Electrochemical devices such as fuel cells, secondary batteries and capacitors are the key to establish a sustainable society and the aim of the present study was to create electroactive composites, which may serve as electrode materials for electrochemical devices, therefore, they should be electrically conductive, porous and electrocatalytically active. To accomplish these objectives we selected two key components, namely cobalt nanoclusters and nitrogen (N)-doped nanostructured carbon. The choice of these constituents was guided by previous works that have shown the beneficial effects of using similar composition on the activity of the electrode materials [1–8]. There is currently an intense interest in the development of non-precious metal electrocatalysts. Although transition metal catalysts, particularly containing Co and Fe, attract much interest as electrocatalysts for oxygen reduction reaction (ORR) [2,3,9–14], N-doped carbon nanostructures have been also reported to show enhanced catalytic activity towards ORR [15–23].

Here we report the synthesis and characterization of the electrocatalysts containing cobalt species and N-doped nanostructured carbon, which were obtained via catalytic chemical vapour deposition (CCVD) at 600, 700 and 800 °C using Mg–Co–Al layered double hydroxides (LDHs) and acetonitrile as starting materials. We

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demonstrate that thermal decomposition of organic compound containing nitrogen (acetonitrile) in the presence of transition metal (cobalt) is a simple method of carbonization and N-doping, whereas LDHs are inexpensive metal precursors for the preparation of carbon nanostructures [4,24–27]. Contrary to the previous works, we used as-prepared LDHs, which were obtained under mild hydrothermal conditions, e.g. at room temperature, in air, and with short ageing, without calcination and reduction before CCVD. Selection of cobalt as one of the components in the electroactive composites has a big advantage because it can perform two catalytic functions, in the formation of carbon nanostructure during the synthesis of the composites, and towards oxygen reduction during the application of the electrocatalysts [4,9,27].

The present work provides a convenient single-step synthesis method of the electrode materials with ORR activity comparable to those containing Co species deposited on graphene [2] or Pt particles spread on carbon nanotubes [17] and is an important contribution to the formation of carbon nanotubes by application of Co-based LDHs.

2. Experimental

2.1. Materials

Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, JIS special grade), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, JIS special grade), aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, 99.9%), sodium hydroxide (NaOH, JIS special grade), potassium hydroxide (KOH, JIS special grade), acetone ($(CH_3)_2CO$, 99.0%) were purchased from Wako Pure Chemical Industries, Ltd. All chemicals were used as received. Alumina polishing suspension (particle size, 0.35 μm) was purchased from Baikowski International Corporation. Nafion® PFSA Polymer Dispersion DE 2020 was purchased from DuPont Fuel Cells. Nitrogen (N_2, 99.99%) was purchased from Air Water, whereas other gases, e.g. argon (Ar, 99.999%) and oxygen (O_2, 99.8%) were purchased from Suzuki Shokan. Water was purified using a Milli-Q purification system (Millipore).

2.2. Preparation of the composites

Mg–Co–Al LDHs (with Mg:Co:Al atomic ratio of 1.75:0.25:1) were synthesized by a co-precipitation method. Aqueous solutions of sodium hydroxide and a mixture of magnesium, cobalt and aluminium nitrates were simultaneously added dropwise to deionized water at constant pH of 10. Hydrothermal synthesis and ageing were carried out at room temperature for 30 min. Then the slurry was filtered, washed with deionized water and dried overnight at 50 °C.

The composites were prepared as follows: 1 g of Mg–Co–Al LDHs in an alumina boat was placed in a tube furnace and heated under a flow of nitrogen (30 mL min^{-1}) to the required temperature (600, 700 and 800 °C). Then the nitrogen stream was saturated with acetonitrile vapour and the sample maintained at the target temperature for 3 h. The composites were cooled down under a flow of nitrogen.

2.3. Characterization of the composites

Powder X-ray diffraction (XRD) analysis was performed using a MultiFlex Rigaku powder diffractometer with Cu K_α radiation (40 kV, 20 mA). The XRD patterns were recorded in the range of 5–139° at scan rate of 4.8° min^{-1} with a step size of 0.05°. Elemental analysis was carried out using a CHNS analyzer (MICRO CORDER JM10). Thermogravimetric (TG) analysis was performed using a Thermo plus TG8120 (Rigaku) analyzer up to 1000 °C under static air condition with a heating rate of 5 °C min^{-1}. Raman spectroscopic measurements were conducted by 0.7 mW 632.8 nm excitation. Nitrogen adsorption/desorption analysis was carried out at −196 °C using an Autosorb-6B, Quantachrome surface area and pore size analyzer. Prior to volumetric sorption measurement, the samples were preheated and degassed under vacuum at 100 °C for 4 h. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were recorded using an HD-2000 microscope (Hitachi) with an operating voltage of 200 keV. X-ray photoelectron spectroscopic (XPS) measurements were performed using an XPS-7000 spectrometer (Rigaku) equipped with Mg K_α X-ray source.

2.4. Electrochemical measurement

Glassy carbon (GC) was used as a substrate for electrochemical measurements. A GC substrate was polished by aqueous alumina suspension on a polishing cloth, and then cleaned by ultrasonic treatment in Milli-Q water and acetone. The composites (20 mg) were ultrasonically mixed with 1 wt % Nafion suspension (1.5 mL) for 60 min. Then the resulting suspension (5 μL) was spread on a GC disk (5 mm in diameter) and dried in air at room temperature. The composite loading was 0.35 mg cm^{-2}.

Electrochemical measurements were performed with an automatic polarization system (Hokuto Denko, HSV-100) using a conventional three-electrode configuration electrochemical cell. A Pt wire and a $Ag/AgCl/NaCl_{sat}$ were used as a counter and reference electrode, respectively. Cyclic voltammograms were recorded at seep rates of 5, 10, 20, 50, 100 mV s^{-1}. Rotating disk electrode (RDE) measurements were carried out using a dynamic electrode unit (Hokuto Denko, HR-201 and HR-202). Current-potential relations were recorded at a sweep rate of 5 mV s^{-1} with rotation rate from 400 to 1600 rpm. The electrolyte was 0.1 M KOH aqueous solution saturated with either oxygen or argon. The bubbling time with oxygen or argon was roughly 40 min. All the electrochemical experiments were carried out at 25 ± 1 °C. All given potentials are referred to Ag/AgCl/NaCl (sat'd).

3. Results and discussion

3.1. Powder X-ray diffraction and elemental analysis

Fig. 1 shows the XRD patterns of the composites prepared at 600, 700 and 800 °C. XRD analysis reveals that all the composites are composed of several components, which are the products of thermal decomposition of Mg–Co–Al LDHs and acetonitrile. According to XRD results, the composite prepared at 600 °C contains two crystalline phases of cobalt oxide with characteristic XRD reflections at $2\theta = 35.3, 43.5, 61.1°$ [28] and magnesium oxide

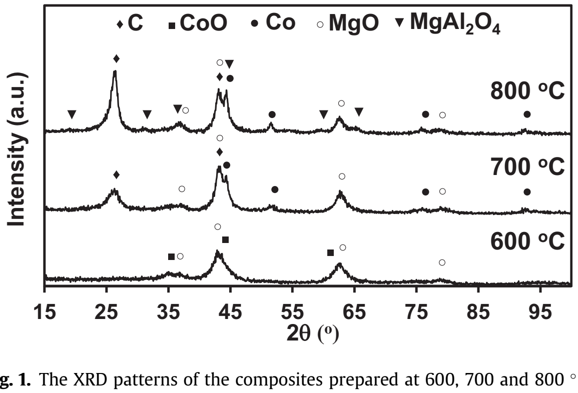

Fig. 1. The XRD patterns of the composites prepared at 600, 700 and 800 °C.