



Preparation of low-platinum-content platinum–nickel, platinum–cobalt binary alloy and platinum–nickel–cobalt ternary alloy catalysts for oxygen reduction reaction in polymer electrolyte fuel cells



Mu Li ^a, Yanhua Lei ^{a, b, *}, Nan Sheng ^{a, b}, Toshiaki Ohtsuka ^a

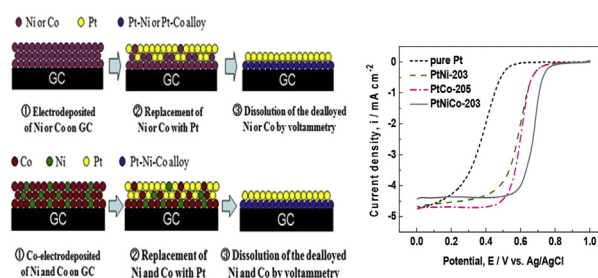
^a Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo, Hokkaido, 060-8628, Japan

^b Center for Advanced Research of Energy and Materials, Faculty of Engineering, Hokkaido University, Kita-13, Nishi-8, Kita-Ku, Sapporo, Hokkaido, 060-8628, Japan

HIGHLIGHTS

- Low-platinum-content Pt–Ni, Pt–Co and Pt–Ni–Co were formed by electrochemical method.
- The total amount of Pt used was significantly reduced.
- The alloys showed obvious enhancement in ORR activity.
- The optimal ORR activity for the three series alloys was obtained individually.
- Electrocatalytic efficiency with an order of PtNiCo > PtCo > PtNi was obtained.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 February 2015

Received in revised form

26 May 2015

Accepted 15 June 2015

Available online 26 June 2015

Keywords:

Oxygen reduction reaction

Electrocatalysts

Pt alloy

Rotating disk electrode

PEFCs

ABSTRACT

A series of low-platinum-content platinum–nickel (Pt–Ni), platinum–cobalt (Pt–Co) binary alloys and platinum–nickel–cobalt (Pt–Ni–Co) ternary alloys electrocatalysts were successfully prepared by a three-step process based on electrodeposition technique and studied as electrocatalysts for oxygen reduction reaction (ORR) in polymer-electrolyte fuel cells. Kinetics of ORR was studied in 0.5 M H₂SO₄ solution on the Pt–Ni, Pt–Co and Pt–Ni–Co alloys catalysts using rotating disk electrode technique. Both the series of Pt–Ni, Pt–Co binary alloys and the Pt–Ni–Co ternary alloys catalysts exhibited an obvious enhancement of ORR activity in comparison with pure Pt. The significant promotion of ORR activities of Pt–Ni and Pt–Co binary alloys was attributed to the enhancement of the first electron-transfer step, whereas, Pt–Ni–Co ternary alloys presented a more complicated mechanism during the electrocatalysis process but a much more efficient ORR activities than the binary alloys.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Polymer-electrolyte fuel cells (PEFCs) are now attracting enormous interest as a kind of prospective new energy, and are expected to be utilized in various applications ranging from

* Corresponding author. Center for Advanced Research of Energy and Materials, Faculty of Engineering, Hokkaido University, Kita-13, Nishi-8, Kita-Ku, Sapporo, Hokkaido, 060-8628, Japan.

E-mail address: yhualai@gmail.com (Y. Lei).

automotive vehicles to stationary and portable devices, due to their high energy efficiency and low air pollution [1]. However, there are still two obstacles of cathode materials restrict PEFCs to their successful commercialization, *i.e.*, the relatively low performance for oxygen reduction reaction (ORR) due to the cathode overpotential and, the high costs resulting from the excessive use of noble metal platinum. Therefore, various research efforts have recently been proposed to resolve these problems [2–9], and it has been reported that to alloy Pt with non-noble metals, such as Fe, Co, Ni, Cr and other transition metals has shown a great promise to lower catalyst cost and improve the ORR activity [10–16]. To date, there are various techniques for the preparation of Pt-based alloy catalysts. Electrodeposition technique appears to be an attractive means of preparing alloy catalyst, not only can it produce uniform metal particle sizes and uniform metal distribution over the substrate with high selectivity from very small to large areas, but also it has various operating parameters to control the amount of deposited metal as well as the desired metal particle sizes and structures [17]. Recently a simple procedure for co-deposition of a range of Pt-transition-metal alloy thin films has been reported [18–24]. Several studies have demonstrated that enhancement of the catalytic activity for ORR belongs to a Pt skin formation in acidic electrolyte. The energy state of electrons in the bulk Pt alloy could modify the electronic structure of Pt skin layers adjacent to the alloy underlayers, because the present of transition metal can lower the Pt d-band center [25–27]. Some experimental and theoretical studies on artificial grown Pt and Co multilayers have revealed significant modification of electronic state of Pt layers more than 6 Å distant from Co layers, and layers of 3d metals such as Fe, Co, and Ni caused the change in the state of conductive electrons in layers of noble metals only over a few tens of angstrom [26,28,29]. It means that thickness of the Pt skin layers should be quite thin and only small amounts of Pt are needed. Therefore, it shows a possible aspect to further reduce the application amounts of Pt, moreover, for most of the Pt atoms in sublayers of the co-deposited catalysts, maybe they do not contribute to the enhancement of catalytic activity for ORR but only play a role as a substrate for those effective a few top layers and possibly could be reduced as well.

In this study, in order to further reduce Pt application amounts and improve Pt service efficiency in electrocatalysts, a series of low-platinum-content Pt–Ni, Pt–Co binary alloys and Pt–Ni–Co ternary alloys were prepared by a three-step strategy based on electrodeposition process, spontaneous Pt replacement process and cyclic voltammetry dealloying process. The ORR electrocatalytic activity was investigated by using rotating disk electrode (RDE), and the kinetic current of ORR was estimated according to the Koutecky-Levich equation. All of the low-platinum-content alloy samples exhibited significant enhancement of the ORR activity than the pure Pt, in which the activities were mainly depended on the kind of initial deposition metals and deposition charge of their metals.

2. Experimental

2.1. Preparation of Pt alloys

The Pt–Ni, Pt–Co and Pt–Ni–Co alloy catalysts were produced by a three-step process. In the case of Pt–Ni and Pt–Co binary alloys, the first step was electrodeposition Ni or Co on a freshly polished glassy carbon (GC) rotating disc electrode (RDE) (5 mm diameter, Pine Instrumentation). An Ag/AgCl/Sat. KCl (SSE) was used as reference electrode and a platinum foil as counter electrode. All the potential in the paper was plotted vs. SSE, potential of which was 0.197 V vs. a Standard Hydrogen Electrode (SHE). The deposition was carried out from 0.25 M

NiCl₂·6H₂O + 0.485 M H₃BO₃ deaerated solution or 0.25 M CoCl₂·6H₂O + 0.485 M H₃BO₃ deaerated solution with the potential set as –0.8 V for Ni or Co deposition, respectively. The total charge density was approximately controlled in the 160–220 mC cm^{–2} range (gradient increased from 160 mC cm^{–2} to 220 mC cm^{–2} per 5–10 mC cm^{–2}) for both Ni and Co deposition. In the second step, the as-prepared series of Ni/GC or Co/GC electrodes which possessed different non-noble metal deposition charge densities were subsequently immersed in a 0.1 M HCl + 10^{–3} M K₂PtCl₆ solution for about 3 min, so that spontaneous Ni or Co replacement by Pt would take place in the surface a few layers of Ni or Co, and Pt-poor alloy precursors of PtNi/GC and PtCo/GC were obtained. The third step was to convert the Pt-poor alloy precursors into their stable surface states and active phases by voltammetric dealloying [30] in 0.5 M N₂ saturated sulfuric acid solution with potential scan from –0.3 V to 1.5 V (100 mV s^{–1}). That is, after the second step, only a few layers close to the surface possessed Pt–Ni or Pt–Co alloy while the sublayers were bulk Ni or Co, however, during the voltammetric dealloying process, the less-noble metal atoms (Ni or Co) from the alloy particle surface and the bulk sublayers were selectively dissolved. Accordingly, a thin Pt skin layer would be formed at the surface of the alloy electrode [26,30]. The Pt–Ni–Co ternary alloy electrocatalysts were produced by a similar three-step process as that for the binary alloy catalysts within the same conditions, with the only difference is in the first step Ni and Co were co-deposited on GC from deaerated 0.25 M NiCl₂·6H₂O + 0.25 M CoCl₂·6H₂O + 0.485 M H₃BO₃ solution at –0.8 V. After the third step, the alloy catalysts electrodes were ready for the following electrochemical analysis. All the procedures were carried out under N₂ atmosphere in a glove box at room temperature (25 ± 1 °C).

2.2. Surface characterizations

Surface compositions of the alloys before the voltammetric dealloying procedure were examined with X-ray photoelectron spectroscopy (XPS, JEOL JPS-9200). The calibration of the binding energy was performed by taking the Au 4f_{7/2} electron peak (E_b = 84.00 eV) with X-ray source of Mg-K_α at 1253.6 eV. The atomic concentration, C_A, of element A on the surface was evaluated on the basis of the following equation [31].

$$C_A = \frac{I_A/S_A}{\sum_n (I_n/S_n)} \quad (1)$$

where I_n is the measured peak intensity for element n and S_n is the relative atomic sensitivity factor (ASF) for that peak. The XPS data on 4f_{7/2} for Pt and 2p_{3/2} for Ni or Co were used in the calculation of metal content. The surface morphology and the composition in the bulk alloy after voltammetric dealloying procedure were measured by using a scanning electron microscope coupled an energy-dispersive spectrometer (SEM-EDS, JEOL JSM-6510LA). The structural and chemical analyses were performed by using a transmission electron microscope (TEM, JEOL JEM-2010F). The Pt content of the binary and ternary alloys before and after voltammetric dealloying procedure was qualified by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 720-ES) and inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer ELAN6000). The samples used for the above characterization were prepared in the same way as those used for electrochemical analysis, only changing RDE to a 1 cm × 1 cm glassy carbon substrate with a Teflon holder limited the deposition area as 0.442 cm².

Download English Version:

<https://daneshyari.com/en/article/7730858>

Download Persian Version:

<https://daneshyari.com/article/7730858>

[Daneshyari.com](https://daneshyari.com)