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Electrocatalytic nitrate reduction on well-defined surfaces of tin-modified platinum, palladium and platinum-palladium single crystalline electrodes in acidic and neutral media

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ABSTRACT

Nitrate anion is one of the main nitrogen-containing-pollutants in groundwater and can be removed using denitrification systems including electrocatalytic systems. Herein we report on electrocatalytic nitrate reduction catalyzed on tin-modified single crystalline electrodes of palladium, platinum and palladium-platinum alloy in acidic and neutral media. We have prepared electrodes with the (111) surface or the (100) surface and modified their surface with tin. Cyclic voltammetry of the electrodes has revealed that the tin-modified alloy (trimetallic) electrodes show higher electrocatalytic activity than the tin-modified platinum or palladium (bimetallic) electrodes, and the catalytic reaction is more efficiently catalyzed on the (100) surface rather than the (111) surface. The tin-modified PdPt(100) electrode shows the highest catalytic activity in acidic media as well as in neutral media. X-ray photoelectron spectroscopy suggests that metallic tin forms on the (100) surface, but divalent tin species on the (111) surface, indicating that a surface alloy of tin may form on the (100) surface, resulting in enhancement of the electrocatalytic activity. Our findings suggest that design and preparation of ternary metallic electrodes with the (100) surface will pave the way to the development of practical systems on electrocatalytic denitrification.

1. Introduction

Nitrate is the main nitrogen-containing pollutant in groundwater and is removed in the natural denitrification process, where nitrate is reduced to harmless dinitrogen gas by denitrifying bacteria [1–5]. Fertilizer-intensive agriculture causes imbalances in the nitrogen cycle and then an increase in the concentration of nitrate ions in groundwater. The excess nitrate ions in groundwater have raised a widespread concern for eutrophication of water reservoirs, and health threats including methemoglobinemia (blue baby syndrome) and cancer [4,5]. Therefore, efficient removal systems of nitrate ions from an aqueous solution containing nitrate are highly required.

Electrocatalytic denitrification is one of the promising approaches to remove nitrate ions from nitrate-contaminated water. A biological denitrification is the most widespread approach, in which bacteria convert NO_3^- to N_2 as long as bacterial growth conditions are maintained. In the biological denitrification system, pathogenic bacteria could be developed, which is a serious issue for the industrial denitrification system [2,4,5]. In contrast, electrocatalytic denitrification systems require electrodes, which are based on inorganic materials and have no concern for the development of the pathogenic bacteria. Furthermore, the electrocatalytic denitrification can be powered by renewable energy such as solar light [6–9] and wind power, leading to environmentally friendly removing nitrate ions from drinking water sources.

Electrocatalytic denitrification systems have been studied using various electrodes such as metals [10,11], binary metals (adatoms and alloys) [12–22], metal nanoparticles [23–26], metal complexes [27–30] and metalloenzymes [3,31–33]. Although the nitrate reduction activity of monometallic electrodes including platinum and palladium has been intensively studied, these monometallic electrodes themselves are known to show poor electrocatalytic activity. To improve their catalytic activity, influences of the combination of other metals [12,21,22,24] or the surface modification with a "promoter" such as tin [13–15,34] on the nitrate reduction activity has been investigated. These treatments are able to accelerate the rate-determining step of the reduction of NO_3^- to nitrite (NO_2^-).

Palladium is one of the most promising metal electrodes for nitrate reduction because palladium is able to produce the most desirable product of N_2 [5,35,36]. Furthermore, the combination of Pt or Pd with a

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promoter of Sn drastically enhances the electrocatalytic activity and the activity of the Sn—Pt or Sn—Pd is enough for practical applications in acidic media [13,15,34,37]. However, from the viewpoint of practical applications such as the decontamination of groundwater, the use of neutral media is relevant [23,38]. Interestingly, Pt(100) catalyzes nitrate reduction in not only acidic but also neutral media, whereas Pt(111) shows the activity only in acidic media [23]. Furthermore, Pt(100) is the most active surface for breaking the N—O bond revealed under UHV conditions [39] and the (100) surface is ideal for a Langmuir-Hinshelwood-type reaction between $(NH_x)_{ads}$ and NO_{ads} [5]. Thus, further studies on the electrocatalytic activity on the (100) surface of metal electrodes would allow us to develop practical electrocatalysts for denitrification.

Herein we report effects of surface structures and compositions of single crystalline electrodes modified with tin on electrocatalytic nitrate reduction activity. We have prepared monometallic platinum and palladium single crystalline electrodes and bimetallic palladium-platinum alloy single crystalline electrodes and then modified their surfaces with tin. In this work, the electrodes with the (111) or the (100) basal plane are used because tin irreversibly adsorbs on Pt(111) and Pt(100) [40]. Electrochemical nitrate reduction on the well-defined surfaces has been studied not only in acidic media but also neutral media to gain insights into developing denitrification electrocatalysts.

2. Experimental

2.1. Materials

Perchloric acid (70%, purity: 99.999%; Sigma-Aldrich Co.), sulfuric acid (96.0%, Wako Pure Chemical Industries, Ltd.), tin(II) chloride dihydrate (97.0%, Kanto Chemical Co., Inc.) and sodium nitrate (99.99, Kanto Chemical Co., Inc.) were purchased and used without further purification. Platinum wires (0.8 mmϕ or 0.5 mmϕ; 99.99% purity) and palladium (0.8 mmϕ or 0.5 mmϕ; 99.99% purity) wires were used for the preparation of single crystalline electrodes.

2.2. Preparation of well-defined single crystalline electrodes

Pt, Pd and PdPt alloy single crystalline beads were prepared based on the procedure reported by Clavilier and co-workers [41–43]. A platinum wire or a palladium wire was annealed in methane-oxygen flame to obtain a single crystalline bead at the end of the wire. For the preparation of Pt—Pd alloy single crystalline beads, the single crystalline bead of Pt was used as a seed crystal as well as the source of Pt, and an amount of Pd was added to the Pt bead in methane-oxygen flame [44–46]. The percentage of Pd in Pt was controlled by the amount of Pd added. In this study, we prepared PdPt alloy electrodes with 3 wt% of Pd in Pt.

The single crystalline beads were oriented using the reflection of a He—Ne laser beam from a (111) facet or a (100) facet on the single crystalline bead, fixed in a poly(methyl methacrylate) resin (Technovit 4004, Heraeus Kulzer), cut in the direction of the (111) facet or the (100) facet, and then polished with diamond slurries to be mirror-finished. The polished single crystalline electrode was annealed in methane-oxygen flame at <1250 °C for 4 h. To confirm the preparation of the single crystalline electrode with a specific orientation, cyclic voltammograms (CVs) were recorded in 0.5 M H_2SO_4 aqueous solution under Ar.

2.3. Electrochemical measurements

The Pt single crystalline electrodes were annealed in H_2–O_2 flame or in the induction coil of an induction heating system (EASY-HEAT, Ambrell model 0224), cooled under Ar, and then immersed in Milli-Q water purged with Ar. The surface of the electrode was covered with Milli-Q water and then transferred to the electrochemical cell for electrochemical measurements. Similarly, Pd and PdPt alloy single crystalline electrodes were annealed using the induction heating system, cooled under H_2—Ar, immersed in Milli-Q water under H_2—Ar, and then transferred to the electrochemical cell under the protection of a droplet of Milli-Q water for electrochemical measurements.

All electrochemical data were recorded on potentiostats (HZ5000 and HZ7000, Hokuto Denko Corp.) using conventional three-electrode systems under Ar (99.999%, HOKKAIDO AIR WATER INC.). Single crystalline electrodes were used as working electrodes. A Ag|AgCl (sat. KCl) electrode with a double junction holder (International chemistry Co., LTD) and platinum foil coated with platinum black were used as the reference electrode and the counter electrode, respectively. Electrolyte solutions were purged with Ar (99.999%) for at least 30 min before measurements. All electrochemical measurements were performed in the hanging meniscus configuration. CVs on nitrate reduction were recorded in a 0.1 M $HClO_4$ aqueous solution containing 0.1 M $NaNO_3$ at a sweep rate of 10 $mV \cdot s^{-1}$ under Ar or in 0.05 M phosphate buffered aqueous solution containing 0.1 M $NaNO_3$ at pH 7.2 at a sweep rate of 50 $mV \cdot s^{-1}$ under Ar. All potentials in the main text are shown against the reversible hydrogen electrode (RHE). The potentials against Ag|AgCl (sat. KCl) were converted to those against RHE using the following equation: E (vs. RHE) $= E$ (vs. Ag|AgCl (sat. KCl)) $+ 0.199 + 0.059 \times$ pH.

The surface modification of single crystalline electrodes with tin was carried out based on a reported procedure [16,19]. The annealed single crystalline electrode covered with a droplet of Milli-Q water was immersed in 0.1 M $HClO_4$ aqueous solution containing $SnCl_2$. The surface coverage was controlled by the $SnCl_2$ concentration (0.1 mM–0.5 mM) and the immersion time (10 s–30 s). After the immersion, the electrode was immediately transferred to an electrochemical cell under the protection of a droplet of the $SnCl_2$ solution. CVs of tin-modified electrodes in the H_{upd} desorption region in 0.5 M H_2SO_4 aqueous solution allowed us to determine the tin surface coverage (θ_{Sn}) using the following equation: $\theta_{Sn} = (Q_H^0 - Q_H)/Q_H^0$, where Q_H^0 and Q_H indicate the Faradaic charges corresponding to the desorption of H_{upd} before and after the tin modification, respectively.

2.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) of single crystalline electrodes was performed on a photoelectron spectrometer XPS7000 (Rigaku). Mg Kα was used as the X-ray source. The peak of C=C at 284.7 eV in the C1s region was used as the internal standard to calibrate the binding energies of the elements.

3. Results and discussion

3.1. Preparation and characterization of single crystalline electrodes of platinum, palladium and palladium-platinum alloy

Platinum, palladium and palladium-platinum alloy single crystalline electrodes were prepared based on the Clavilier method [41–43]. To characterize the prepared electrodes, their CVs were recorded in 0.5 M H_2SO_4 under Ar. Fig. 1 shows CVs of single crystalline electrodes with well-defined (111) surfaces. The CV of the Pt(111) electrode showed adsorption/desorption peaks of underpotentially deposited hydrogen (H_{upd}) at <+0.5 V vs. RHE and a spike involving a phase transition in the sulfate adlayer on Pt(111) surface at around +0.42 V vs. RHE [43]. The CV of the Pd(111) electrode also shows sharp peaks in the potential range from +0.2 to +0.3 V vs. RHE, originating from the sulfate adsorption and desorption [47]. These characteristic features allowed us to confirm the preparation of the well-defined Pt(111) and Pd(111) electrodes.

The PdPt(111) alloy single crystalline electrode with 3 wt% of Pd in Pt was prepared, based on a previously reported method [44–46]. The well-defined single crystalline electrode was confirmed using cyclic voltammetry in 0.5 M H_2SO_4 under Ar (Fig. 1). The peak intensity of