



Reduction of nitrate on electrochemically pre-reduced tin-modified palladium electrodes



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ABSTRACT

The electrochemical pretreatment of Sn-modified Pd electrodes at the negative potentials of ≤ -0.2 V vs. Ag/AgCl (sat. KCl) enhanced their electrocatalytic properties for the reduction of nitrate. Namely, the nitrate reduction current increased by several times depending on the potentials for the nitrate reduction and the pretreatment, and the product selectivity for the formation of N_2 increased from 29% for the as-prepared (untreated) electrodes to 51%. The STM, XPS and cyclic voltammetric measurements revealed that the following structural changes were induced by the pretreatment. (1) Spontaneously adsorbed divalent tin was reduced to zero-valent tin. (2) The hydrogen adsorption and absorption ability of Pd was almost lost while the surface Sn fraction decreased. (3) Primary particles of ca. 30 nm observed on a Pd and an as-prepared Sn/Pd electrode were reconstructed to larger particles of 45 nm. Based on these results on the structural change and the literature on d-band filling in binary metal systems, it was concluded that the surface Sn/Pd alloy was formed, and thereby the surface electronic structure was changed. This accelerated N–O bond cleavage and decreased the hydrogenation ability.

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1. Introduction

Noble metal-based binary metal electrodes often exhibit a higher electrocatalytic activity than single noble metal electrodes. Particularly the tin-modification of platinum and/or palladium can drastically enhance their activity for important reactions such as the reduction of nitrate and the fuel cell reactions. The reduction of nitrate has received considerable attention from the viewpoint of the electrochemical remediation of nitrate-contaminated water systems [1–3]. In our previous studies [4–6], we reported that tin-modified Pt and Pd electrodes (Sn/Pt and Sn/Pd) showed an extremely high catalytic activity for nitrate reduction, while unmodified Pt and Pd showed a negligible activity. Particularly, the maximum activity of Sn/Pd obtained at a Sn coverage greater than 0.65 is the highest among the already reported electrodes [7–17]. The study of the oxidation of methanol has a long history, and still is one of the most important current issues because this is the anode reaction of the methanol–fuel cell. It is well known that the Sn/Pt electrodes enhanced the electrocatalytic activity of Pt by 50–100 times for this reaction [18–21].

During the study of such binary electrodes, however, we often face the problem that data are not very consistent with those reported by other groups. For example, the addition of Sn to Pt electrodes always enhanced the catalytic activity for the oxidation of methanol, but the magnitude of the enhancement varied from report to report. Similar phenomena were also observed for Sn modified noble metal electrodes for the reduction of nitrate, although the data variation was not as significant compared to the oxidation of methanol. There are several factors to consider which affect the electrocatalytic properties of binary metals. Surface composition is the most important factor. Particularly, in the case when a second metal, which is easily oxidized when exposed to air, was used, the surface composition often changed under the reaction conditions from that when it was determined because the electrode was usually exposed to air between the characterization and reaction experiments. However, in the case of the Sn modified noble metal electrodes, this is not the case because Sn is very stable and is not removed from the surface even if it was exposed to air. We have reported that the surface coverage of Sn is an important factor in determining the activity for the reduction of nitrate [4–6]. The activity also depends on the Pd layer thickness [6]. In the present study, it will be demonstrated that an electrochemical pretreatment, or reduction of the as-prepared Sn/Pd, prior to the electrode reaction is another important factor and has an enhancement effect on the reduction of nitrate.

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2. Experimental

2.1. Materials

Tin (II) chloride dihydrate, perchloric acid, and sodium nitrate obtained from Kanto Chemicals were of reagent grade. All aqueous solutions were prepared by using Milli-Q water (18.3 Mohm cm at 25 °C) and were used after sufficient deaeration with argon of 5 N purity.

2.2. Preparation of Pd and tin-modified electrodes

Glass slides (Matsunami Glass Ind., Ltd. BK7, 20 mm × 13 mm × 0.7 mm³), sonicated in soap water (5 vol.% solution of CONTRAD 70) for 1 h and then rinsed with water, were used as underlying substrates of the Pd film electrodes. After the plasma treatment at 20 mA under about 2 Pa for 300 s, 75 nm of Au and 5 nm of Pd (JEOL Co., Japan) were successively deposited onto the glass slides under about 2 Pa by a sputtering instrument (JFC-1600, JEOL Co., Japan). The electrode potential was repeatedly scanned in the range of –0.2 to 1.2 V at the scan rate of 0.05 V s^{–1} until a reproducible cyclic voltammogram was recorded. Although the Au substrate was used, this Pd film electrode is simply cited as a Pd electrode or more simply Pd.

The Pd electrodes were immersed in a 0.12 mM SnCl₂ + 0.1 M HClO₄ solution for various periods of time ranging from 2 to 20 min, followed by rinsing with copious amounts of water. The tin was spontaneously adsorbed onto the electrode surface by this procedure. This prepared tin modified electrode is labeled as the as-prepared Sn/Pd.

2.3. Electrochemistry

All electrochemical measurements were performed in a three-electrode cell with a platinized Pt counter electrode and a Ag/AgCl (sat. KCl) reference electrode. All potentials in the text are referred to this reference. The cyclic voltammetric measurements were conducted in an Ar-filled glove box by an HZ-5000 automatic polarization system (Hokuto Denko, Japan). The electrolysis at a constant potential for the product analysis was performed in the previously described Nafion membrane-separated cell [5,6].

2.4. Product analysis

The concentrations of NO₃[–], NO₂[–], and NH₄⁺ in a solution were determined by ion chromatography and that of hydroxylamine (NH₂OH) by flow injection analysis [5,6]. The gaseous composition was analyzed by a Canon-Anelva model M-201QA-TDM quadrupole mass spectrometer for the entire gas phase collected in a pre-evacuated sampling vessel after the reaction [5,6].

2.5. X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectra (XP spectra) were obtained using a Rigakudenki model XPS-7000 X-ray photoelectron spectrometer with monochromic Mg-Kα radiation at 25–300 W. The takeoff angle was 90°. The Au 4f_{7/2} emission was used as the internal reference to determine the binding energies of the elements.

2.6. Scanning tunneling microscopy (STM)

All STM images were obtained using a Nanoscope III STM (Digital Instruments, USA) under ambient laboratory conditions. For imaging, mechanically cut Pt–Ir tips were used. The instrument was equipped with a low-current converter MMS–STMLC. All

images were acquired at a constant tunneling current (10–100 pA) with bias voltages of 0.7–1.0 V.

3. Results and discussion

3.1. Reduction of nitrate on tin modified Pd electrodes

3.1.1. Tin-coverage dependence of electrocatalytic activity of as-prepared Sn/Pd electrodes

Fig. 1 shows cyclic voltammograms of the Pd electrodes in 0.1 M HClO₄ before and after the tin modification. The hydrogen wave of the as-prepared Sn/Pd (dashed curve) is much smaller than that of Pd (dotted curve), showing the blocking of the adsorption sites for hydrogen atoms by the tin. The tin coverage, θ_{Sn} , was determined from the charges obtained by integrating the oxidation waves of Pd and as-prepared Sn/Pd, Q_{H}° and Q_{H} , respectively, and the equation of $\theta_{\text{Sn}} = (Q_{\text{H}}^{\circ} - Q_{\text{H}}) / Q_{\text{H}}^{\circ}$. For the particular case shown in Fig. 1, $\theta_{\text{Sn}} = 0.89$. It should be mentioned that the determined θ_{Sn} is not very correct because the contribution of adsorbed hydrogen atoms in the bulk Pd cannot be neglected. However, the contribution is considered to be much smaller than that of the bulk Pd because of the Pd layer thickness (5 nm). Therefore, the present θ_{Sn} should be taken as the value at first approximation. The cyclic voltammogram of the as-prepared Sn/Pd (Fig. 1, dashed curve) corresponds to the reference for electrochemically pretreated Sn/Pd electrodes described later. It should be emphasized that the hydrogen wave still appeared for the as-prepared Sn/Pd electrode, which almost completely disappeared after the pretreatment (see Section 3.2 (3) for details).

As described in the experimental section, electrodes with different θ_{Sn} values were prepared by changing the adsorption time of tin. The electrocatalytic activity on the apparent area basis increased with the increasing θ_{Sn} from 0.32 to 0.82 (Fig. 2). As shown in the inset of Fig. 2, however, the nitrate reduction current at –0.1 V did not significantly increase until θ_{Sn} reached 0.45, beyond which it abruptly increased and reached the maximum at around 0.8. At an extremely high θ_{Sn} , it had a tendency to decrease. Such a θ_{Sn} dependence is consistent with the previously reported one for Sn/Pd electrodes, which were prepared by electrochemical Pd deposition followed by the spontaneous tin adsorption [6].

3.1.2. Pretreatment effect on the electrocatalytic activity of Sn/Pd electrode

As described in a previous report [6], the electrocatalytic activity is dependent on the tin-coverage and Pd layer thickness. We

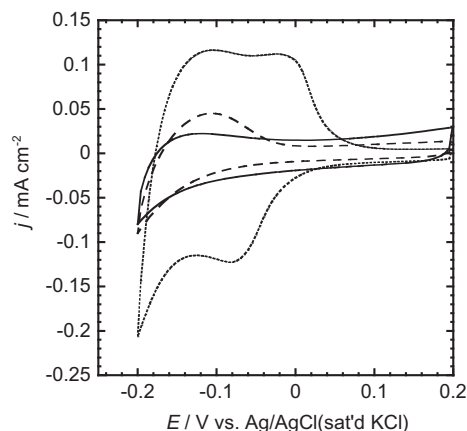


Fig. 1. Cyclic voltammograms of (dotted curve) Pd, (dashed curve) as-prepared Sn/Pd, and (solid curve) pretreated Sn/Pd electrodes in 0.1 M HClO₄ at the scan rate of 0.05 V s^{–1}. Tin was adsorbed by immersing a Pd electrode in a 0.12 mM SnCl₂ solution for 15 min. The tin coverage was 0.89. The electrochemical pretreatment was conducted at –0.35 V for 60 s.

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