Electrochemical Reduction of Nitrate Ions on Tin-Modified Platinum and Palladium Electrodes

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The tin-modified platinum and palladium-deposited gold (Sn/Pt and Sn/Pd/Au) electrodes have exhibited a higher electrocatalytic activity for the reduction of nitrate than any electrode so far reported in the literature. Ammonium ions were predominantly formed on Sn/Pt, while N_2O and/or N_2 were the most likely main products on Sn/Pd/Au.

The nitrate concentration in ground water has recently increased due to over-fertilizing. Although the nitrate itself is not considered to be very toxic, the nitrite formed from it by the reducing action of intestinal bacteria causes serious health risks such as methemoglobinemia (blue baby syndrome). In addition, *N*-nitrosamines formed from the nitrite at stomach pH levels are believed to cause cancer. Therefore, the removal of nitrate from the drinking water, most of which is produced from ground water, is one of the most important technologies to be developed. The electrochemical reduction of the nitrate has been conducted using various electrodes such as metals,[1,2] binary metals (adatoms[3–7] and alloys[8]), metal complexes,[9–12] and synthetic diamonds.[13,14] Although the nitrate reduction was examined only from a mechanistic aspect in early studies, it was recently studied based on an environmental concern. The best electrode so far reported is Cu/Pd,[3] which showed the highest catalytic activity along with the high yield of harmless nitrogen gas, which is the best product among the possible NO_2^-, NO, N_2O, N_2, NH_3, etc., although the N_2 yield decreased with increasing activity. We now report the electrocatalytic behavior of Sn-modified Pt and Pd electrodes for the reduction of the nitrate, which are found to show higher activity than the Cu/Pd electrode.

A commercially available platinum thin film electrode on a quartz wafer (MAXTEK) was cleaned by immersion in mixed concentrated nitric and sulfuric acids followed by a sufficient rinse with water. The cyclic voltammogram was taken to confirm the cleanliness of the electrode surface and to determine the Pt surface area from the charge required for the oxidation of the adsorbed hydrogen ($Q_H{}^0$). The polycrystalline gold thin film on a quartz wafer similarly treated was used as the substrate electrode for the palladium deposition. The deposition was performed at 0.425 V in 1 mM K_2PdCl_4 + 0.1 M $HClO_4$. The deposition amount and the surface coverage of Pd were estimated from the deposition charge and $Q_H{}^0$, respectively. The surface coverage of the palladium used in this study was ca. 0.5. The platinum or palladium-deposited gold electrode was immersed in a 0.025 mM $SnCl_2$ solution for various periods of time. The electroreduction of nitrate was conducted in 0.01 M and 0.1 M $NaNO_3$ + 0.1 M $HClO_4$. Reagent grade chemicals and Milli-Q water were used for the preparation of the aqueous solutions. All the electrochemical measurements were performed in solutions sufficiently deaerated with 5N purity argon prior to use. The potentials in the text are referred to a Ag/AgCl(sat'd KCl) electrode. Nitrate, nitrite and ammonium ions were analyzed by the flow injection analysis (FIA).

Figure 1 shows the cyclic voltammograms for the reduction of nitrate ions on the Sn-modified platinum (Sn/Pt) electrodes. The reduction current was observed at potentials below 0.1 V or in the so-called hydrogen region. The hydrogen evolution reaction was very slow compared to the reduction of nitrate so that the reduction current due to the former reaction was negligibly small for the scale in Figure 1. The reduction current is strongly dependent on the surface coverage of Sn (θ_{Sn}) as shown in Figure 1. The Sn-coverage on platinum was calculated using the equation of $\theta_{Sn} = (Q_H{}^0 - Q_H)/Q_H{}^0$, where Q_H represents the charge required for the oxidation of the adsorbed hydrogen after the adsorption of tin. The platinum electrode not modified with Sn showed no catalytic activity for the reduction of nitrate. On the bare Pt electrode, the formation of the adsorbed hydrogen was also partially suppressed. The Sn-coverage dependence of the reduction current at −0.1 V during the potential cycling at the sweep rate of 0.01 V s^{-1} is shown in Figure 2a. With increasing Sn-coverage, the reduction current increased and reached a maximum value of 3.6 mA cm^{-2} at around $\theta_{Sn} = 0.35$, beyond which the activity tends to decrease. Data at higher θ_{Sn} values than 0.60 were not yet obtained because such electrodes were hard to prepare under the tin-concentration conditions of 0.025–0.25 mM. The reduction current is slightly dependent on the nitrate concentration. In 0.1 M $NaNO_3$ + 0.1 M $HClO_4$, the maximum current was 4.3 mA cm^{-2}.

The Sn-modified palladium/gold (Sn/Pd/Au) electrodes also show the electrocatalytic activity in the hydrogen region similar to the Sn/Pt electrodes. The reduction current at −0.1 V for the Sn/Pd/Au electrodes in 0.1 M $NaNO_3$ + 0.1 M $HClO_4$ was plotted as a function of the surface coverage of Sn in Figure 2b. The Au electrode modified with Sn as well as the Pd/Au and Au electrodes

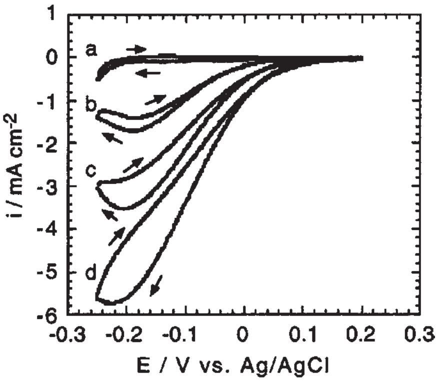

Figure 1. The reduction of the nitrate ions on Sn/Pt electrodes with various Sn-coverages in 0.01 M $NaNO_3$ + 0.1 M $HClO_4$. (a) $\theta_{Sn} = 0$, (b) $\theta_{Sn} = 0.08$, (c) $\theta_{Sn} = 0.21$ and (d) $\theta_{Sn} = 0.34$. The sweep rate was 0.01 V s^{-1}.

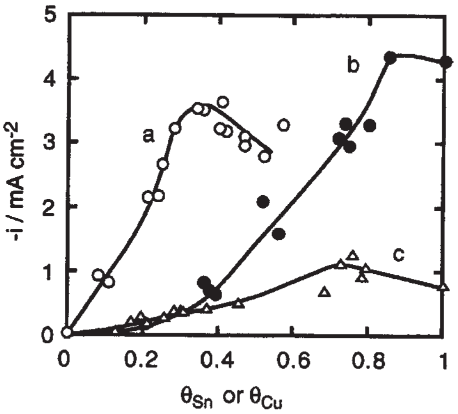

Figure 2. Sn- and Cu-coverage dependences of the reduction current at −0.1 V during the potential sweep of 0.01 V s^{-1}. Electrodes: (a) Sn/Pt, (b) Sn/Pd/Au, (c) Cu/Pd/Au. Electrolyte solutions: (a) 0.01 M $NaNO_3$ + 0.1 M $HClO_4$, (b,c) 0.1 M $NaNO_3$ + 0.1 M $HClO_4$.

unmodified with Sn showed no catalytic activity for the reduction of nitrate. The activity increased with increasing Sn-coverage and reached the maximum value of ca. 4.4 mA cm^{-2} at around $\theta_{Sn} = 0.82$. A similar dependence was also obtained in 0.01 M $NaNO_3$ + 0.1 M $HClO_4$, although the maximum reduction current was approximately 2.8 mA cm^{-2}.

As mentioned above, the Cu/Pd electrode showed the highest catalytic activity for this reaction among the electrodes so far studied in the literature. In order to compare the catalytic activity of the Sn-modified electrodes with that of the Cu/Pd electrode under the same conditions, we have prepared the Cu/Pd/Au electrode by electrochemically depositing copper onto Pd/Au (the surface coverage of Pd was 0.5–1.0) from 0.1 mM $CuCl_2$ + 0.1 M $HClO_4$. Because it was found that a part of the deposited copper was dissolved when the circuit was open unlike the tin on the Pt and Pd/Au electrodes, the deposition solution was exchanged with a nitrate solution under potential control to avoid any dissolution. After the reduction of the nitrate, the surface coverage of copper (θ_{Cu}) was determined from the charge due to the anodic stripping of copper from the electrode surface. The electrocatalytic activity of the electrode thus prepared for the reduction of the nitrate was close to that previously reported by Vooys et al.:[3] at 0.02 V vs. RHE, for example, −5.5 mA cm^{-2} at $\theta_{Cu} = 0.72$ in this study and −3.4 mA cm^{-2} at $\theta_{Cu} = 0.63$ in 0.5 M $HClO_4$ in ref. 3. Figure 2c shows the Cu-coverage dependence of the reduction current at −0.1 V vs. Ag/AgCl in 0.1 M $NaNO_3$ + 0.1 M $HClO_4$. The activity increased with θ_{Cu} and the maximum one was obtained at $\theta_{Cu} = 0.7$–0.8 similar to Sn/Pd/Au. Such a behavior (higher activity at larger Cu-coverages) is also similar to that reported previously,[3] although no data were shown for $\theta_{Cu} \geq 0.63$. As shown in Figure 2c, the activity of Cu/Pd/Au is about one-fourth of those for Sn/Pt and Sn/Pd/Au. Therefore, the Sn-modified electrodes show a much higher activity than the Cu-modified Pd electrode.

The nitrate ions and solution products such as NO_2^- and NH_4^+ were analyzed by FIA. The selectivity, defined as the ratio of the mole of the product formed to the mole of NO_3^- reacted, was then determined for each product. For the reduction at −0.1-−0.2 V on Sn/Pt ($\theta_{Sn} = 0.25$–0.35), the average selectivity for the formation of NH_4^+ was 0.86 ± 0.08 at 15–52% conversion. The NO_2^- selectivity was always below 0.01. Thus, the main product from the nitrate is NH_4^+ on Sn/Pt. On the other hand, a much lower production of NH_4^+ (0.15 ± 0.01) was observed on Sn/Pd/Au ($\theta_{Sn} \geq 0.88$). The selectivity for NO_2^- was also low (0.04 ± 0.01). To identify the other products, we have calculated the average number of electrons consumed for the products ($n_{AV,others}$) using the following equation.

$$n_{AV,others} = \frac{Q_{total} - 2FN_{NO_2} - 8FN_{NH_3}}{F(N_{total} - N_{NO_2} - N_{NH_3})} \qquad (1)$$

where the N's represent the number of moles reacted or produced for the compounds shown in the subscript, Q_{total} is the total charge, and F is the Faraday constant. The number was determined to be 3.8–4.9, showing that N_2O and/or N_2 are the most likely main products on Sn/Pd/Au. The direct detection of these compounds is now under investigation.

In summary, we have found that the tin-modified platinum and palladium electrodes showed high electrocatalytic activity for the reduction of nitrate, while unmodified electrodes had no activity. The activity was dependent on the Sn-coverage. The maximum activities obtained at 0.35 for Sn/Pt and at >0.80 for Sn/Pd/Au are compatable to each other, and are larger than the Cu/Pd electrode, which was so far regarded to be the highest. The main products are ammonium ions on Sn/Pt, and N_2O and/or N_2 on Sn/Pd/Au.

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