

**Preparation of Highly Active Binary Metal
Electrocatalysts for Reduction of Nitrate Ions by
Successive Adsorption of Precursor Ionic Species on
Gold**

K. Shimazu, K. Tada, and T. Kawaguchi
Graduate School of Environmental earth Science,
Hokkaido University
Sapporo 060-0810, JAPAN

Groundwater, which is main source of drinking water, is significantly contaminated worldwide with nitrates due to over-fertilizing, the excreta of cattle and industrial effluent. In the human body, nitrate is reduced to toxic nitrite, which causes cyanosis and breathing problems. Therefore, the development of denitrification technology is currently required. Electrochemical denitrification is receiving increased attention because it has superior advantages compared with the currently used or proposed technologies such as biological denitrification, ion-exchange, and catalytic reduction [1]. In this paper, we report a novel preparation method for highly active Pt-Sn and Pd-Sn binary metal electrocatalysts for the reduction of nitrate by successive adsorption of tin and corresponding novel metal complex on Au(111) [2,3].

The Au(111) electrode was prepared by evaporating gold (200nm) on a slide glass. The gold electrodes were immersed in 25 μ M SnCl₂ + 0.1 M HClO₄ for more than 900 sec, followed by sufficient rinsing with water. Then the electrode was immersed in 1 mM K₂PtCl₆ or Na₂PdCl₄ solution for various periods to control the adsorption amount of novel metal. The adsorbed complex was reduced in a fresh 0.1 M HClO₄ solution by applying a potential of 0 V until the reduction current became zero. The electrodes thus prepared are denoted as the Pt/Sn/Au and Pd/Sn/Au electrode.

Quartz crystal microbalance (QCM) measurements during the adsorption of tin revealed that the maximum ratio of the adsorbed Sn to the surface Au, which is obtained when tin is adsorbed without accompanying the strongly adsorbed species (adsorbed oxygen, electrolyte anion and solvent), is 1.0. In order to estimate the number of surface Pt or Pd atoms from the amount of adsorbed hydrogen atoms, the cyclic voltammograms were taken in a 0.1 M HClO₄ solution for the electrodes immersed in the metal complex solution for various periods after subsequent reduction. The number of the surface atoms reached maximum values at the adsorption times of \geq 1200 min and \geq 80 min for PtCl₆²⁻ and PdCl₄²⁻, respectively. The maximum numbers correspond to 0.30 and 0.87 in the ratio of Pt to Au and Pd to Au, respectively, taking the roughness factor into account. The Pt to Sn ratio were separately determined using X-ray photoelectron spectroscopy to be 0.30. Based on these results, the maximum (in Pt or Pd) surface ratio between these three surface components is concluded to be 1 : 1 : 0.30 for Au : Sn : Pt and 1 : 1 : 0.87 for Au : Sn : Pd. It should be emphasized that the maximum numbers of the surface Pt and Pd atoms correspond to the extremely low loading of 0.18 μ g-Pt cm⁻² and 0.29 μ g-Pd cm⁻², respectively.

The electrocatalytic activity for the reduction of nitrate was examined in 0.01 M NaNO₃ + 0.1 M HClO₄ by the cyclic voltammetry. Although Pt and Pd electrodes not coated with Sn and a Au electrode coated with Sn had no activity, both Pt/Sn/Au and Pd/Sn/Au electrodes showed

extremely high catalytic activity, showing that the increase in the activity is due to the synergetic effect of Sn and Pt or Pd. The activity was dependent on the surface composition. The maximum activities (activity is defined as the current at -0.1 V during the negative-going potential scan at a sweep rate of 0.01 V s⁻¹), which were obtained at Pt/Sn = 0.30 and Pd/Sn = 0.60, are -2.7 and -3.5 mA cm⁻², respectively. Although Pt or Pd loading is extremely low, these activities are approximately the same as those reported at Sn-modified Pt and Pd electrodes (-3.2 and -2.8 mA cm⁻², respectively), which are the highest activities among the electrodes so far examined. At Pd/Sn/Au, this high reduction current maintained over several hours. This means that the Pd/Sn/Au electrode is very stable and does not suffer deactivation due to poisoning and/or rearrangement of the surface atoms. This feature is very important for its use as a practical electrocatalyst and was never observed for Sn-modified Pt, Pd and Rh electrodes.

The products formed during constant potential polarization experiments in 0.1 M NaNO₃ + 0.1 M HClO₄ were analyzed by ion chromatography, flow injection analysis and a quadrupole mass spectrometer. At Pt/Sn/Au (Pt/Sn = 0.30), ammonium ion was predominantly formed (97 %) with a trace amount of nitrite at -0.1 V. At Pd/Sn/Au (Pd/Sn = 0.7), on the other hand, the main product was N₂ (37%) at -0.15 V. The remaining products are NH₄⁺ (30.8 %), N₂O (23.2 %) and NO₂⁻ (9.3 %). The N₂ selectivity of 37 % obtained here is approximately the same as the maximum value (40 %) so far reported in an electrochemical system, which was obtained at Cu-Pd electrodes [4]. Because the Pd/Sn/Au electrode showed much higher catalytic activity than the Cu-Pd electrode despite of a much lower Pd loading, the Pd/Sn/Au electrode is the best at present among all electrodes so far reported.

References

- [1] K. Rajeshwar, J. G. Ibanez, Environmental Electrochemistry-Fundamentals and Applications in Pollution Abatement, Academic Press, San Diego, 1997.
- [2] K. Shimazu, T. Kawaguchi, K. Tada, J. Electroanal. Chem., 529 (2002) 20.
- [3] K. Tada, T. Kawaguchi, K. Shimazu, J. Electroanal. Chem., submitted.
- [4] A. C. A. de Vooys, R. A. van Santen, J. A. R. van Veen, J. Mol. Catal., 154 (2000) 203.