Enhanced Hydrogen Adsorption/Desorption Characteristic of Ta_2O_5-coated Pt Electrode Prepared by Electrodeposition of Ta and the Subsequent Calcination

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Ta_2O_5-coated Pt electrodes prepared by electrodeposition of Ta and the subsequent calcination were found to possess a remarkably enhanced adsorption/desorption characteristic of hydrogen atoms in sulfuric acid solutions compared with bare Pt electrodes. This enhancement can be explained by a spillover–reverse spillover of hydrogen atoms adsorbed at Pt sites over the Ta_2O_5 surface.

The adsorptive and electrochemical properties of supported metal catalysts are largely different from those of the individual components,[1] because support effects including a strong metal-support interaction (SMSI) act in the supported metal catalyst systems.[2] A transport phenomenon of hydrogen and oxygen-containing species on the surface of catalysts,[1a,2] so-called "spillover," has been often observed on the supported metal catalysts such as Pt/C,[1a,3] Pt/SiO_2,[4] Pt/Al_2O_3,[5] Pt/WO_3,[6] Pt/TiO_2,[7] $Pt–TiO_2/Ti$,[8] and $Pt/SO_4{}^{2-}–ZrO_2$.[9] In the spillover process, the reactive species adsorbed at the active sites of the metal diffuse onto the inactive surface of the supporting material across the phase boundary between active and inactive surfaces. Spillover behavior over Pt/C catalyst in electrochemical systems was reported by Bagotzky et al.[1b] and Liu et al.[3d] They have pointed out that hydrogen spillover phenomenon plays an important role in electrocatalytic reactions in Pt/C systems.

Bagotzky and Skundin also reported anomalous hydrogen adsorption/desorption behavior on Pt/high-melting metals (i.e., Ti, Ta, Zr, and Nb) in 0.5 M H_2SO_4 solutions.[10] There have been many researches concerning spillover phenomena of hydrogen atoms over various metal oxide-supported metal catalysts in catalytic and electrocatalytic systems. However, no studies have been conducted for tantalum oxide-coated Pt electrodes. Tantalum oxide which possesses a high corrosion resistance under environmentally severe conditions has been widely investigated to develop anodes for high-efficiency oxygen and/or ozone production.[11,12] In the course of our attempts to prepare the tantalum oxide-coated Pt (Ta_2O_5/Pt) electrode with a view to developing novel anode materials for electrochemical ozone production,[12] we found unusual hydrogen adsorption/desorption voltammograms at the prepared electrodes in H_2SO_4 solutions. In the present communication, we will report the unique hydrogen adsorption/desorption feature of the Ta_2O_5/Pt electrodes.

Electrodeposition of Ta was carried out in an electrochemical cell made of glassy carbon. A smooth Pt plate (geometric area: 1.1 cm^2) working, a Pt spiral wire counter and a Ta wire quasi-reference electrodes were used. The cell filled with LiF–NaF (60:40 mol %) molten salts containing K_2TaF_7 (20 mass %)[13] was placed in a chamber of IR electric furnace (RHL-P610C, ULVAC-RIKO, Inc.) equipped with a temperature controller (TPC-1000, ULVAC-RIKO, Inc.) and heated at 800 °C under argon (Ar) gas atmosphere. Electrodeposition of Ta onto Pt substrate was carried out in a controlled-current mode of $-80\,mA\,cm^{-2}$ for 10 min. After the electrodeposition, the obtained Ta-electrodeposited Pt (Ta/Pt) plate electrode was introduced into a muffle furnace (STR-12K, Isuzu Seisakusho Co., Ltd.) and calcinated at 600 °C for 30 min in air atmosphere to prepare Ta_2O_5/Pt electrode. An excess tantalum oxide overlayers exfoliated from the Pt substrate during the calcination process. X-ray diffraction (XRD, X'Pert-Pro-MRD, PANalytical) measurements were performed to identify the surface composition of thus-prepared electrodes. Figure 1 shows typical XRD pattern and the peak assignments.[14] It was found that tantalum oxide deposited on the Pt substrate was Ta_2O_5 (orthorhombic crystalline), and thus the prepared electrode was identified as a Pt partially covered with thin insulating deposits of Ta_2O_5.[15] The amount of Ta_2O_5 coated over the Pt surface was estimated to be ca. $0.18\,mg\,cm^{-2}$ by X-ray fluorescence analysis (X-ray Fluorescence Spectrometer JSX-3220ZS, JEOL). Cyclic voltammetry was used to investigate the electrochemical behavior of the prepared Ta_2O_5/Pt electrodes in 50 mM H_2SO_4 solutions at room temperature (23 ± 2 °C). A Pt spiral wire and a potassium chloride-saturated silver|silver chloride (Ag|AgCl|KCl (sat.)) were used as the counter and the reference electrodes, respectively.

Figure 2 shows typical cyclic voltammograms (CVs) obtained at bare Pt plate (dotted curve, a) and Ta_2O_5/Pt plate (solid curve, b) electrodes in the potential range between −0.22 and 1.3 V vs Ag|AgCl|KCl (sat.) in Ar-saturated 50 mM H_2SO_4 solution (The ordinate is indicated as the current density

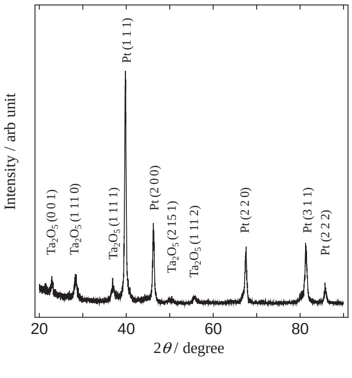

Figure 1. XRD pattern obtained for the surface of tantalum oxide-coated Pt electrode.

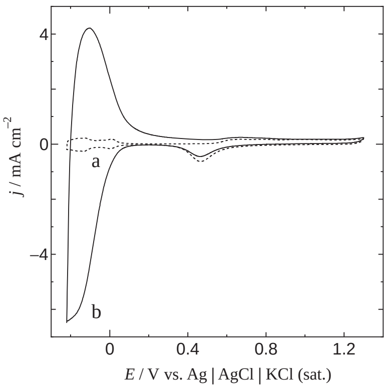

Figure 2. CVs obtained at (a) bare Pt and (b) Ta_2O_5/Pt electrodes in Ar-saturated 50 mM H_2SO_4 solution. Potential scan rate was 100 mV s^{-1}. Current densities in CVs were calculated using the geometric area of each electrode.

in which the observed current was normalized with apparent geometric surface areas of the electrodes). For the bare Pt electrode, well-defined current peaks due to the reduction of surface platinum oxide layer and the hydrogen adsorption/desorption waves were observed at ca. 0.5 V, and ca. 0 and −0.15 V, respectively. In the case of curve b, the electroactive Pt surface area (i.e., platinum surface area exposed to the solution) estimated from the charge consumed in the reduction process of surface platinum oxide layer is by ca. 17% smaller than that of the bare Pt electrode owing to the partial coating of the Pt surface with the insulating Ta_2O_5. On the contrary, one can see that the hydrogen adsorption/desorption waves appear with significantly enhanced intensity at the Ta_2O_5/Pt electrode. The amounts of charge consumed in the adsorption (Q_{ads}) and desorption (Q_{des}) processes of hydrogen atoms at Pt and Ta_2O_5/Pt plate electrodes were estimated and they are summarized in Table 1. As can be seen from Table 1, the values of both Q_{ads} and Q_{des} at the Ta_2O_5/Pt electrode are far larger than those obtained at the bare Pt electrode (by ca. 23 and 21 times, respectively). This unusual enhancement in the hydrogen adsorption/desorption amount may be ascribable to the "spillover" phenomenon of hydrogen atoms over the Ta_2O_5/Pt electrode: That is, in the cathodic scan, hydrogen atoms adsorbed at electroactive Pt sites via one-electron reduction of protons may get across the phase boundary zone and diffuse into the Ta_2O_5 sites and the reverse process (i.e., reverse spillover) may take place in the anodic scan.

The charge ratio Q_{ads}/Q_{des} can be considered as a measure of reversibility in the adsorption/desorption process of hydrogen; a value of 1.0 was obtained for the bare Pt electrode. Malevich et al.[8a] have reported that the Q_{ads}/Q_{des} value of Pt–TiO_2/Ti electrodes changes between 1.4 and 2.0 depending on the Pt amount in the deposits. Contrasting to this, the Q_{ads}/Q_{des} ratio calculated for the Ta_2O_5/Pt electrode was found to be almost unity (ca. 1.1, Table 1), which indicates that the Ta_2O_5/Pt electrode prepared in this study possesses higher reversibility for hydrogen adsorption/desorption behavior, i.e., the spillover and reverse spillover processes occur reversibly.

Table 1. Charge consumed in the adsorption/desorption processes of hydrogen atoms onto/from each electrode used in Figure 2

Electrodes	Q/mC cm^{-2}	
	Adsorption (Q_{ads})	Desorption (Q_{des})
bare Pt	0.42	0.42
Ta_2O_5/Pt	9.67	8.77

In summary, we have prepared the Ta_2O_5/Pt electrode by an electrodeposition of Ta onto Pt substrate and the subsequent calcination process. It exhibited a remarkably enhanced hydrogen adsorption/desorption feature, which is ascribed to the so-called "spillover–reverse spillover" effect of hydrogen atoms. The present composite electrode is expected to possess a prominent potential for the storage (and liberation) of hydrogen atoms on (and from) its surface. The studies regarding this point and also quantitative estimation of the spillover and reverse spillover processes are currently in progress.

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