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Catalytic Electrooxidation of Formaldehyde at Ta$_2$O$_5$-modified Pt Electrodes

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The Ta$_2$O$_5$-modified Pt electrode, which was prepared by electrodeposition of Ta on a Pt electrode from 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPTFSI) ionic liquid and subsequent calcination, possesses excellent electrocatalytic activity toward the oxidation of formaldehyde to CO$_2$ in 0.5 M H$_2$SO$_4$ solution compared with the bare Pt electrode. This significant improvement in catalytic performance may be attributed to the strong metal–oxide interaction as well as hydroxide spillover effect of the modified electrode. A possible reaction mechanism is proposed.

Nowadays, the electrooxidation of small organic molecules, such as formic acid, formaldehyde, and methanol, has received much attention due to their use as promising fuels in fuel cells.[1–4] The simple molecular structure of formaldehyde (HCHO) has promoted its use as a model to gain insight into the processes of the electrooxidation of small organic molecules which is a subject of long-term interest in the development of fuel cell technology.[5,6] The study of electrochemical oxidation of formaldehyde is also important for the full understanding of methanol oxidation as it is produced as the intermediate compound by partial oxidation of methanol.[6–10]

It has been reported that formaldehyde exists in aqueous solution in hydrated form, methylene glycol [H$_2$C(OH)$_2$], and is oxidized at Pt electrodes via two parallel (i.e., direct and indirect) pathways.[5–7] In the direct pathway, formaldehyde is directly oxidized via short-lived intermediate(s) to CO$_2$ as the final product.

$$H_2O + HCHO \rightleftarrows H_2C(OH)_2 \rightarrow H_2COO_{ad} \rightarrow CO_2 \quad (1)$$
$$\downarrow \qquad \uparrow$$
$$HCOOH$$
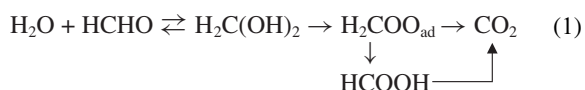
On the other hand, the indirect pathway involves the formation of a poisonous intermediate (CO$_{ad}$) that adsorbes on the electrode surface and is finally oxidized to CO$_2$ at higher potential.

$$H_2O + HCHO \rightleftarrows H_2C(OH)_2 \rightarrow CO_{ad} \rightarrow CO_2 \quad (2)$$
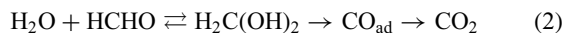
Therefore, much attention has been devoted to surface modification which allows the direct oxidation of formaldehyde to CO$_2$ to occur preferentially, resulting in the mitigation of Pt poisoning.[4,8,11] In this communication we report that the modification of Pt electrode with Ta$_2$O$_5$ largely enhances the electrooxidation of formaldehyde. The modification was carried out by electrodeposition of Ta metal on a Pt electrode from BMPTFSI ionic liquid followed by calcination of the Ta-deposited Pt electrode.

The tantalum electrodeposition onto Pt plate electrodes (area: 6.0 mm^2) was performed by controlled potential electrolysis at −2.2 V vs. Pt wire quasi-reference electrode for 100 s at
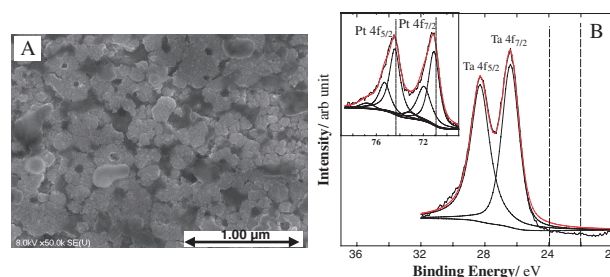

Figure 1. (A) SEM micrograph of Ta$_2$O$_5$-modified Pt and (B) XPS spectrum obtained for 4f energy levels of Ta on the Ta$_2$O$_5$-modified Pt electrode surface. The inset of Figure 1B shows the XPS spectrum for Pt 4f at the Ta$_2$O$_5$-modified Pt electrode. The dotted lines correspond to the binding energies of elemental Ta or Pt (4f$_{7/2}$ and 4f$_{5/2}$).

100 °C in BMPTFSI containing 0.2 M TaF$_5$ and 0.2 M LiF.[12] The Ta-deposited Pt electrode was successively washed with acetone, ethanol, and hot 2-propanol and then calcinated in an electric furnace at 600 °C for 30 min under air atmosphere to prepare the tantalum oxide (TaO$_x$)-modified Pt electrode.

Figure 1A shows a typical SEM image of the TaO$_x$-modified Pt electrode. The TaO$_x$ deposit inhomogeneously covers the Pt electrode surface with interstices among the particles which allows the easy access of the solution species to the underlying Pt surface through the modifier matrix. The XPS spectrum of the TaO$_x$-modified Pt electrode surface is presented in Figure 1B. The binding energies of 4f levels of Ta are shifted to higher values (i.e., 28.3 (4f$_{5/2}$) and 26.4 eV (4f$_{7/2}$)) compared to those (24 (4f$_{5/2}$) and 22 eV (4f$_{7/2}$)) of elemental Ta, indicating that the deposited Ta exists in a cationic state rather than in an elemental state: Ta$_2$O$_5$.[13] The deconvolution of the Pt 4f signal (inset of Figure 1B) reveals the presence of three different Pt species. The most intense doublet with the binding energies of 71.2 (Pt 4f$_{7/2}$) and 74.3 eV (Pt 4f$_{5/2}$) is ascribed to metallic Pt. Peaks at 72.0 and 75.2 might be assigned to Pt^{2+} as in either combination with OH, Pt(OH)$_2$,[14] or other oxygen species like PtO.[15] The third doublet found at 73.1 and 76.4 eV appears to be Pt^{4+}, possibly as PtO$_2$.[14] Compared with the peak (4f$_{7/2}$) at 70.9 for elemental Pt,[15] the peak (4f$_{7/2}$) for the Ta$_2$O$_5$-modified Pt is shifted positively by 0.3 eV, reflecting strong interaction between Pt and Ta$_2$O$_5$ which is due to the induced positive charge on the Pt surface interacting with the TaO$_x$.[16] Such an electronic interaction may result in electrocatalysis of formaldehyde oxidation (mentioned below).

From the reversible cyclic voltammetric responses obtained for the [Fe(CN)$_6$]$^{4-}$/[Fe(CN)$_6$]$^{3-}$ redox couple at the bare and Ta$_2$O$_5$-modified Pt electrodes in 0.1 M KNO$_3$ solution, it was found that about 30% of the Pt surface was covered by Ta$_2$O$_5$ deposit.[17] In Figure 2, the comparison of two couples of well-
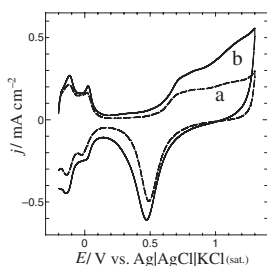
Figure 2. Cyclic voltammograms (CVs) measured at (a) bare Pt and (b) Ta_2O_5-modified Pt electrodes in N_2-saturated 0.1 M H_2SO_4 solution. Potential scan rate: $100\,mV\,s^{-1}$.

Figure 3. (A) CVs obtained at (a) bare Pt and (b) Ta_2O_5-modified Pt electrodes in 0.5 M Ar-saturated H_2SO_4 solution containing 0.1 M HCHO. Potential scan rate: $10\,mV\,s^{-1}$. (B) Amperometric j–t curves for HCHO oxidation at the individual electrodes (a and b) at 0.4 V in the same solution.

defined peaks corresponding to a hydrogen adsorption–desorption observed at both the bare Pt and Ta_2O_5-modified Pt electrodes demonstrates a significant enhancement of the hydrogen adsorption–desorption response at the modified electrode, although by the modification of the Pt surface with Ta_2O_5 the real Pt surface area is smaller than the bare Pt electrode as mentioned above. A similar phenomenon was reported by Sata et al. for a Ta_2O_5-modified Pt electrode which was prepared by the electrodeposition of Ta from LiF–NaF molten salt containing K_2TaF_7.[18,19] They explained this enhancement using a hydrogen spillover–reverse spillover mechanism. Thus, the present observation can also be considered to reflect the hydrogen spillover effect. Furthermore, interestingly, the anodic current corresponding to the Pt oxide monolayer formation and the cathodic current corresponding to the Pt oxide reduction were also observed to be larger at the Ta_2O_5-modified Pt electrode than at the bare Pt electrode. This current enhancement is thought to be due to OH^- spillover at the Ta_2O_5-modified Pt electrode as reported by Boskovic et al.[20]

Figure 3A shows the CVs measured at the bare and Ta_2O_5-modified Pt electrodes in 0.5 M Ar-saturated H_2SO_4 containing 0.1 M formaldehyde. During the forward potential sweep, a peak current appears at ca. 0.64 V and is attributed to the oxidation of CO_{ad}, which is the oxidation intermediate of the formaldehyde, to CO_2 on the Pt surface, and one shoulder at ca. 0.5 V can be considered to correspond to the direct oxidation of formaldehyde to CO_2 which is retarded by the strong adsorption of an intermediate species (CO_{ad}) on the Pt surface[7,8,21] (curve a). By scanning the potential to a more positive value, all the CO_{ad} species are oxidized and consequently the Pt surface becomes clean. That is the reason why in the reverse scan an increased anodic peak was observed at ca. 0.4 V corresponding to the complete oxidation of formaldehyde to CO_2 at the clean Pt surface. On the contrary, it is obvious from curve b that the modification of Pt electrode by Ta_2O_5 greatly improves its catalytic activity for formaldehyde oxidation, i.e., the onset potential shifts by ca. 0.11 V to the negative compared to that at the bare Pt electrode. In addition, the peak current density corresponding to the electrooxidation of formaldehyde at the modified Pt electrode is, as a whole, considerably higher than that at the bare Pt electrode. The amperometric j–t curves show that the Ta_2O_5-modified Pt supports a higher oxidation current than the bare Pt (Figure 3B).

Formaldehyde is thought to be and intermediate product of CH_3OH oxidation, and it is oxidized via the formation of HCOOH (or COOH) to CO_2. From previous research on the
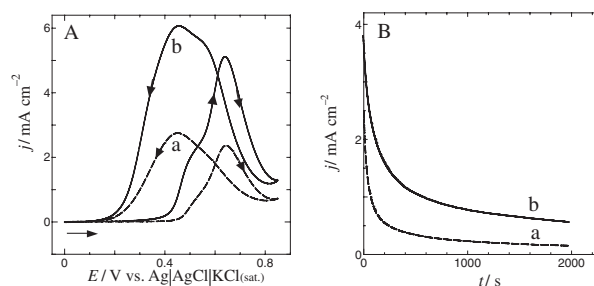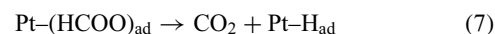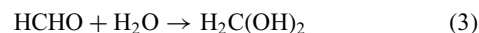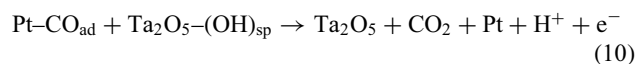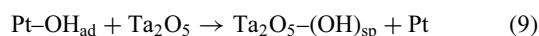
oxidation of methanol, formic acid, and formaldehyde at various electrodes[7,8,16,21–24] and the present study, a possible reaction mechanism for the formaldehyde oxidation at the Ta_2O_5-modified Pt electrode is given as follows:

$$HCHO + H_2O \rightarrow H_2C(OH)_2 \tag{3}$$

$$H_2C(OH)_2 + Pt \rightarrow Pt\text{–}(H_2COO)_{ad} + 2H^+ + 2e^- \tag{4}$$

$$Pt\text{–}(H_2COO)_{ad} \rightarrow Pt\text{–}(HCOO)_{ad} + H^+ + e^- \tag{5}$$

$$Pt\text{–}(H_2COO)_{ad} \rightarrow Pt\text{–}(HCOOH)_{ad} \tag{6}$$

$$Pt\text{–}(HCOO)_{ad} \rightarrow CO_2 + Pt\text{–}H_{ad} \tag{7}$$

$$Pt\text{–}(HCOOH)_{ad} \rightarrow Pt\text{–}CO_{ad} + H_2O \tag{8}$$

where the subscript "ad" shows the adsorbed species. The electrooxidation of formaldehyde is greatly affected by the adsorbed hydrogen (eq 7) and CO (eq 8). The adsorbed hydrogens are mostly oxidized to H^+ ions at potentials more anodic than 0 V (Figure 2). The enhanced performance of the Pt electrode by the modification with Ta_2O_5 could be attributed to the following aspects; the d–d metal–oxide interaction[22] between Pt and Ta_2O_5 and the hydroxide spillover effect.[20] Some reports[16,23,24] inferred that the interacting metal/metal oxide may alter the electronic properties of catalytically active Pt metal which leads to the formation of the so-called "weakly" adsorbed state of CO_{ad} on Pt sites. In the present case, the electronic interaction between Pt and Ta_2O_5, which is evident from XPS, is thought to reduce the bonding strength between Pt and CO_{ad}, resulting in the decrease in the coverage of CO_{ad} on the Pt surface and finally the enhanced catalytic oxidation of formaldehyde. On the other hand, oxygen species that may generate via OH spillover from Pt substrate to Ta_2O_5 surface might contribute to the enhanced oxidation of CO_{ad} like $RuPt/TiO_2/C$[23] catalyst through the bifunctional mechanism,[24] as can be written as follows:

$$Pt\text{–}OH_{ad} + Ta_2O_5 \rightarrow Ta_2O_5\text{–}(OH)_{sp} + Pt \tag{9}$$

$$Pt\text{–}CO_{ad} + Ta_2O_5\text{–}(OH)_{sp} \rightarrow Ta_2O_5 + CO_2 + Pt + H^+ + e^- \tag{10}$$

where the subscript "sp" shows the species generated by hydroxide spillover. These processes may lead to the generation of active sites on the Pt surface for the electrooxidation of formaldehyde.

In conclusion, the Ta_2O_5-modified Pt electrode shows a significantly improved catalytic activity for the electrooxidation

of formaldehyde to CO_2 compared with the bare Pt electrode. The observed excellent electrocatalysis may originate from the electronic as well as hydroxide spillover effects.

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