Hydrous Ruthenium Oxide-Supported Pt and Pt-Ru Catalysts for the Oxidation of Methanol

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Binary Pt-Ru/C is a promising CO-tolerant anode catalyst for use in direct-methanol fuel cells (DMFCs). The promotion effect has been mainly discussed based on so-called "bifunctional effect" [1] or "ligand effect" [2] or mixture of both. The bifunctional mechanism proposes that Ru promotes the oxidation of the strongly bound CO_{ad} on Pt by supplying an oxygen source ($Ru-OH_{ad}$). According to the ligand effect, the energy level of the catalyst is changed so that the binding strength of CO_{ad} is weakened, thereby reducing the oxidation overpotential.

The actual state of the active ruthenium component is still a point of discussion. Some investigations suggest that hydrous ruthenium oxide is one of the active components for oxidation of the carbonaceous intermediates adsorbed on the catalyst surface in binary Pt-Ru black catalysts [3-5]. When Pt or Pt-Ru was deposited on hydrous ruthenium oxide, however, no significant electrochemical activity was found [6].

$Pt/RuO_2·xH_2O$ catalysts were prepared by the liquid-phase reduction of H_2PtCl_6. H_2PtCl_6 in an aqueous solution was completely reduced with 1-propanol at 87°C to Pt particles dispersed on commercial $RuO_2·xH_2O$ ($[Pt]:[RuO_2·xH_2O] = 3:7, 5:5$ and $7:3$).

$Pt-Ru/RuO_2$ xH_2O catalysts were prepared on the basis of a preparation method of Pt-Ru/C by Poizo et. al. [7]. $(NH_3)_2PtCl_6$ and $RuNO(NO_3)_x$ in an aqueous solution ($[(NH_3)_2PtCl_6]/[RuNO(NO_3)_x] = 1$) were completely reduced with sodium borohydride at 110°C to Pt-Ru particles dispersed on commercial $RuO_2·xH_2O$ ($[Pt]:[Ru]:[RuO_2·xH_2O] = 1:1:8, 1:1:4, 1:1:2, 1:1:1, 2:2:1$ and $4:4:1$).

The working electrode was a thin film electrode composed of a mirror polished Glassy Carbon rod (0.196 cm^2 exposed surface) modified with 40 µg of the active material. A beaker-type electrochemical cell equipped with the working electrode, a platinum mesh counter electrode, and an Ag/AgCl reference electrode was used. Electrochemical measurements were conducted at 25°C. All electrode potentials will be referred to the RHE scale corrected for the temperature effect. Oxidation of pre-adsorbed carbon monoxide (CO_{ad}) was measured by CO_{ad} stripping voltammetry in 0.5 M H_2SO_4 solution at a scan rate of 10 mV s^{-1}. The electrochemical oxidation of methanol was characterized by the steady state current density at 0.5 V in 1 M CH_3OH + 0.5 M H_2SO_4 solution.

The CO_{ad} stripping voltmmograms were measured for $Pt/RuO_2·xH_2O$ catalysts with various loadings. The CO_{ad} oxidation potential for any $Pt/RuO_2·xH_2O$ catalyst significantly decreased compared with that for the Pt/C catalyst. It suggests that no CO_{ad} species was observed on $RuO_2·xH_2O$. These data support the bifunctional effect: $RuO_2·xH_2O$ promotes the oxidation of the strongly bound CO_{ad} on Pt by supplying an oxygen source.

Pt mass specific activities for the methanol oxidation were compared in $Pt/RuO_2·xH_2O$ catalysts with various loadings. The specific activities of $Pt/RuO_2·xH_2O$ catalysts were independent of Pt-loadings and about 7 times as high as that of the Pt/C catalyst. No catalytic activity of $RuO_2·xH_2O$ was observed for the methanol oxidation.

X-ray diffraction patterns of $Pt-Ru/RuO_2·xH_2O$ catalysts were attributed to the face-centered cubic crystalline structure of Pt. The lattice parameter of the cubic phase was smaller than that of the Pt cubic phase. It suggests a fcc solid solution of Pt and Ru. The lattice parameter was reduced by the introduction of Ru in the Pt fcc structure.

The CO_{ad} stripping voltmmograms were measured for $Pt-Ru/RuO_2·xH_2O$ catalysts with various loadings. The CO_{ad} oxidation potential for any Pt-$Ru/RuO_2·xH_2O$ catalyst significantly decreased compared with that for the Pt/C catalyst, similar to that for the $Pt/RuO_2·xH_2O$ catalyst.

Pt mass specific activities for the methanol oxidation were compared in $Pt-Ru/RuO_2·xH_2O$ catalysts with various loadings. The specific activities of Pt-$Ru/RuO_2·xH_2O$ catalysts with high loadings ($[Pt]/[RuO_2·xH_2O] = 2/1$ and $4/1$) were almost as high as that of the $Pt/RuO_2·xH_2O$ catalyst, while, in the case of $[Pt]/[RuO_2·xH_2O] = 1/4$, the specific activity is about 3 times as high as that of the $Pt/RuO_2·xH_2O$ catalyst. It suggests that binary Pt-Ru gives higher catalytic activity than Pt for highly dispersed Pt or Pt-Ru, while not highly dispersed Pt gives the similar activity to binary Pt-Ru because of the bifunctional effect of $RuO_2·xH_2O$.

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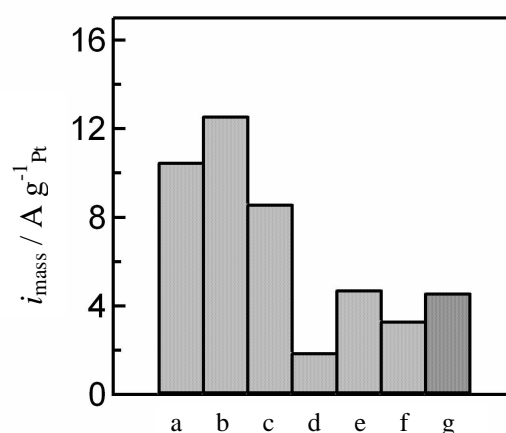[7] A. Poizo, R. F. Silva, M. De Francesco, F. Cardellini, L. Giorgi, *Electrochim. Acta* **48**, 225 (2002).

Figure 1 Pt mass specific activities of Pt-Ru/$RuO_2·xH_2O$ with various loadings ($[Pt]:[Ru]:[RuO_2·xH_2O] =$ (a) 1:1:8, (b) 1:1:4, (c) 1:1:2, (d) 1:1:1, (e) 2:2:1 and (f) 4:4:1) and (g) $Pt/RuO_2·xH_2O$ ($[Pt]:[RuO_2·xH_2O] = 1:1$) for the methanol oxidation at 0.5 V in 1 M CH_3OH + 0.5 M H_2SO_4 solution.