

Catalytic Activity of Platinum on Ruthenium Electrodes with Modified (Electro)chemical States

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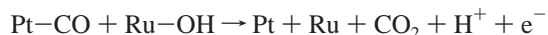
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Using Pt on Ru thin-film electrodes with various (electro)chemical states designed by the sputtering method, the effect of Ru states on the catalytic activity of Pt was investigated. The chemical and electrochemical properties of Pt/Ru thin-film samples were confirmed by X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry. In addition, Pt nanoparticles on Ru metal or oxide for an actual fuel cell system showed an effect of Ru states on the catalytic activity of Pt in methanol electrooxidation. Finally, it was concluded that such an enhancement of methanol electrooxidation on the Pt is responsible for Ru metallic and/or oxidation sites compared to pure Pt without any Ru state.

Introduction

Excellent electrochemical activity of platinum for oxidation of hydrogen or methanol provides potential for use as an anode in solid-state polymer membrane fuel cells using hydrogen or methanol as a fuel.^{1–3} In addition, such fuel cells have recently received interest because of their numerous advantages and applications. However, at low temperature, pure platinum is readily poisoned by CO, an impurity in the hydrogen gas and a byproduct in methanol electrooxidation. Accordingly, to enhance its electrochemical activity for hydrogen or methanol electrooxidation by eliminating the CO poisoning effect, a variety of efforts have been reported to design Pt-based catalysts by alloying or mixing platinum with ruthenium element on the basis of electronic effects and a bifunctional mechanism.^{4–10}

In particular, according to the bifunctional mechanism, the CO-poisoned platinum can be regenerated by the reaction of surface CO with oxygen species associated with elements such as ruthenium and osmium to yield CO₂.^{11,12} It has been well-known that the CO-poisoned platinum is regenerated via reaction of surface CO with O-type species associated with ruthenium to generate CO₂.^{13–29} Due to the fact that the bonding energy of Ru–O is similar to that of Pt–C, Ru in the PtRu easily oxidizes the CO intermediate to CO₂ by the bifunctional mechanism as in the following equation:



Such oxophilic Ru sites covered by RuOH are the source of oxygen required for surface CO removal, and as a result, Ru-modified electrocatalysts for methanol electrooxidation have excellent catalytic activity. It is likely that the Ru metallic state would play a key role as an oxygen source to oxidize CO. However, it has been reported that hydrous ruthenium oxides in the Pt–RuO₂ electrode play an important role in mediating proton transport during methanol electrooxidation.^{30–33} Due to the contribution of RuO_xH_y to proton and electron conducting,

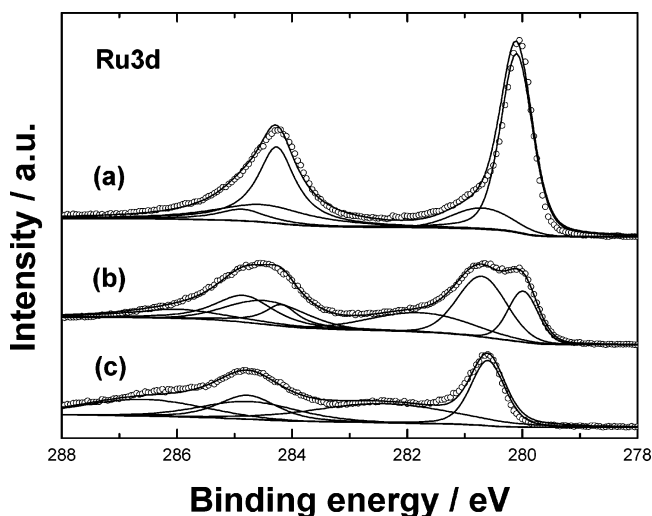


Figure 1. X-ray photoelectron spectra (XPS) of Ru 3d of (a) metallic dominant, (b) mixed, and (c) oxidative Ru thin-film electrodes fabricated by the sputtering deposition method.

a mixed-phase nanosized electrocatalyst containing Pt metal and RuO_xH_y may have considerable potential for use in methanol electrooxidation.

In this paper, to investigate the effect of Ru states on the catalytic activity of Pt, Pt/Ru thin-film electrodes with various (electro)chemical states were fabricated by sputtering deposition. The chemical and electrochemical states of the electrodes were confirmed by X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry. In addition, the Pt/Ru nanosized catalysts prepared by the chemical synthesis method were compared with Pt/Ru thin-film electrodes deposited by the sputtering method.

Experimental Section

The various Ru thin-film electrodes were fabricated using Ru metal target in an atmosphere of only Ar, a mixture of Ar and O₂, and only O₂, respectively. The Pt catalyst layers on Ru electrodes were deposited by means of a Pt metal target under only Ar. The base and working pressure were less than 1 ×

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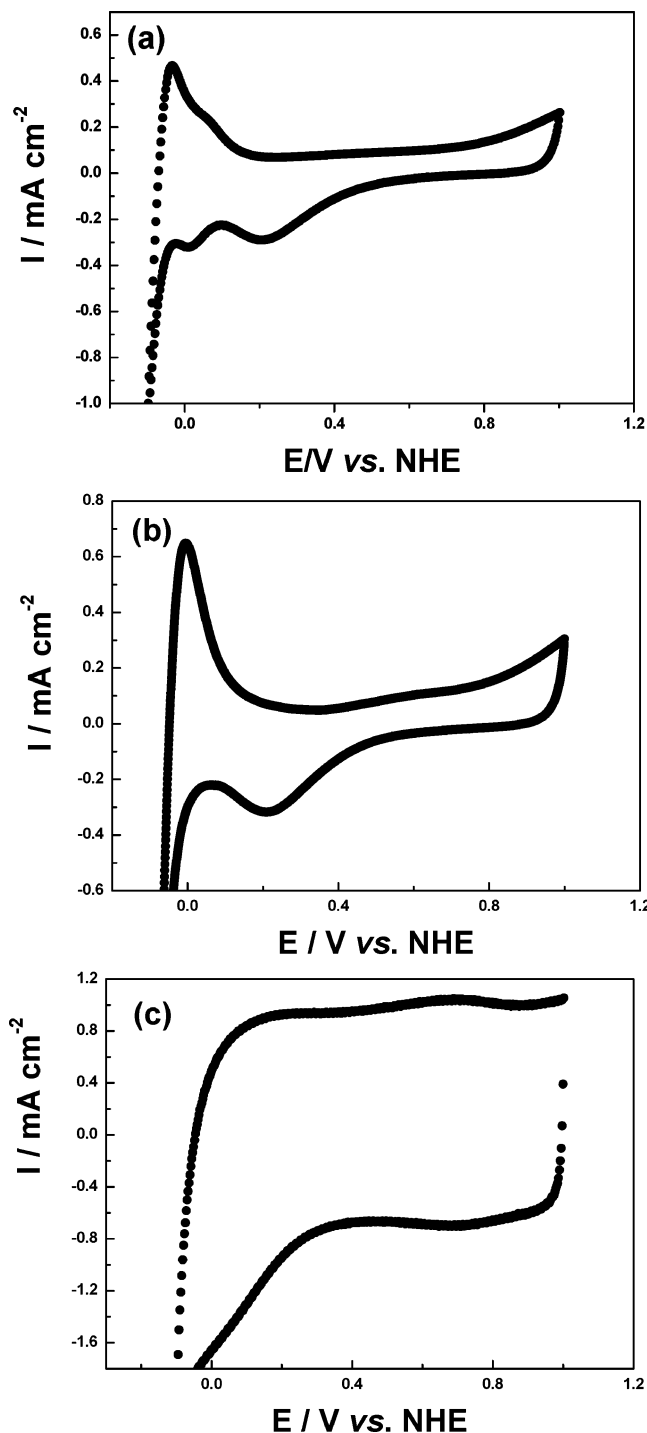


Figure 2. Cyclic voltammograms of (a) metallic dominant, (b) mixed, and (c) oxidative Ru thin-film electrodes in 0.5 M H_2SO_4 at a scan rate of 50 mV/s.

10^{-6} and 1×10^{-2} Torr, respectively, for all films examined. Pt/Ti/Si was used as a substrate. To investigate the effect of Ru states on methanol electrocatalysis of Pt in an actual system, Pt nanosized catalysts supported on Ru metal and oxide particles were synthesized at room temperature by the conventional reduction method using a Pt salt ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Aldrich Chemical Co.) and NaBH_4 as the reducing agent.^{1,4,34,35}

To analyze and compare the surface chemical states of the samples, X-ray photoelectron spectroscopy (XPS) was carried out using a VG Scientific photoelectron spectrometer. Structural analyses of Pt-based catalysts were carried out using an X-ray diffractometer equipped with a $\text{Cu K}\alpha$ source. Electrochemical

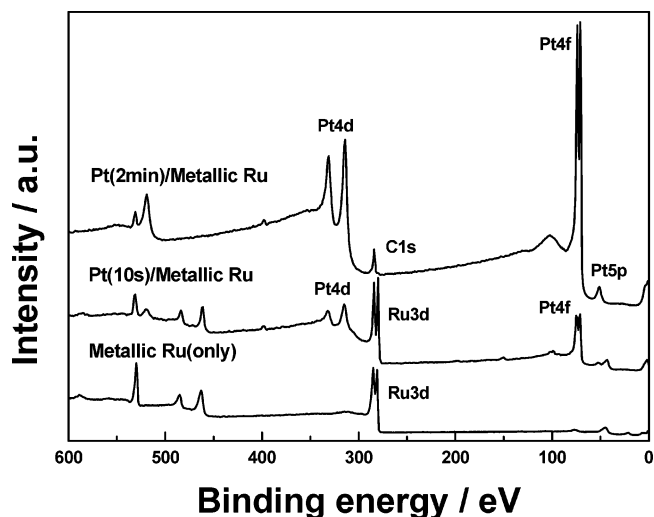


Figure 3. X-ray photoelectron spectra (XPS) of Pt layers on a metallic dominant Ru thin-film electrode as a function of Pt deposition time of 0 s, 10 s, and 2 min.

measurements were investigated using a three-electrode cell at room temperature. The prepared thin-film electrodes were used as a working electrode. Pt wire and Ag/AgCl (in saturated KCl) were used as a counter and a reference electrode, respectively. Electrochemical characteristic curves in 0.5 M H_2SO_4 or 2 M $\text{CH}_3\text{OH} + 0.5$ M H_2SO_4 , which were stirred constantly and purged with nitrogen gas, were recorded. All potentials are reported versus the normal hydrogen electrode (NHE) in this paper.

Results and Discussion

To investigate effect of Ru states on catalytic activity, Ru thin-film electrodes were prepared by means of the sputtering method. Figure 1 a–c corresponds to a Ru 3d spectrum of thin-film electrodes sputtered in an atmosphere of only Ar, a mixture of Ar and O_2 , and only O_2 , respectively. In Figure 1a, the Ru thin-film electrode sputtered in an atmosphere of only Ar shows the most metallic ruthenium which appears as a spin–orbit doublet at 279.9 eV (Ru $3d_{5/2}$) and 284.1 eV (Ru $3d_{3/2}$) with the area ratio of 1.5. However, as shown in Figure 1b, the Ru thin-film electrode sputtered in an atmosphere of a mixture of Ar and O_2 consists of oxidation states of both RuO_2 (281.2 and 285.4 eV) and RuO_3 (282.7 and 286.9 eV) as well as metallic states. The XPS spectra (Figure 1c) of a Ru thin-film electrode sputtered in an atmosphere of only O_2 displays only oxidation states without metallic states. Accordingly, this means that well-defined Ru thin-film electrodes with metallic dominant (90% of Ru^0), mixed (metallic (30% of Ru^0) and oxidation (70% of Ru^{n+})), and oxidation (100% of Ru^{n+}) states are prepared by sputtering deposition. The characteristic curves of Ru thin-film electrodes in 0.5 M H_2SO_4 are shown in Figure 2. In the CVs of modified Ru thin-film electrodes of Figure 2, the changes of capacitance are attributed to changes in the thickness of the double layer, which is more likely to be due to a portion of conducting oxide film. The cyclic voltammograms (CVs) of the electrodes exhibit electrochemical properties of metallic dominant, mixed, and oxidation Ru states. Both the XPS spectrum of Figure 1 and CVs of Figure 2 indicate clear evidence of well-defined Ru thin-film electrodes having various electrochemical states. However, to compare the catalytic activity of Pt on modified Ru states, Pt layers were deposited on the Ru thin-film electrode as a function of deposition time. Figure 3 shows XPS spectra of metallic dominant Ru electrodes deposited by

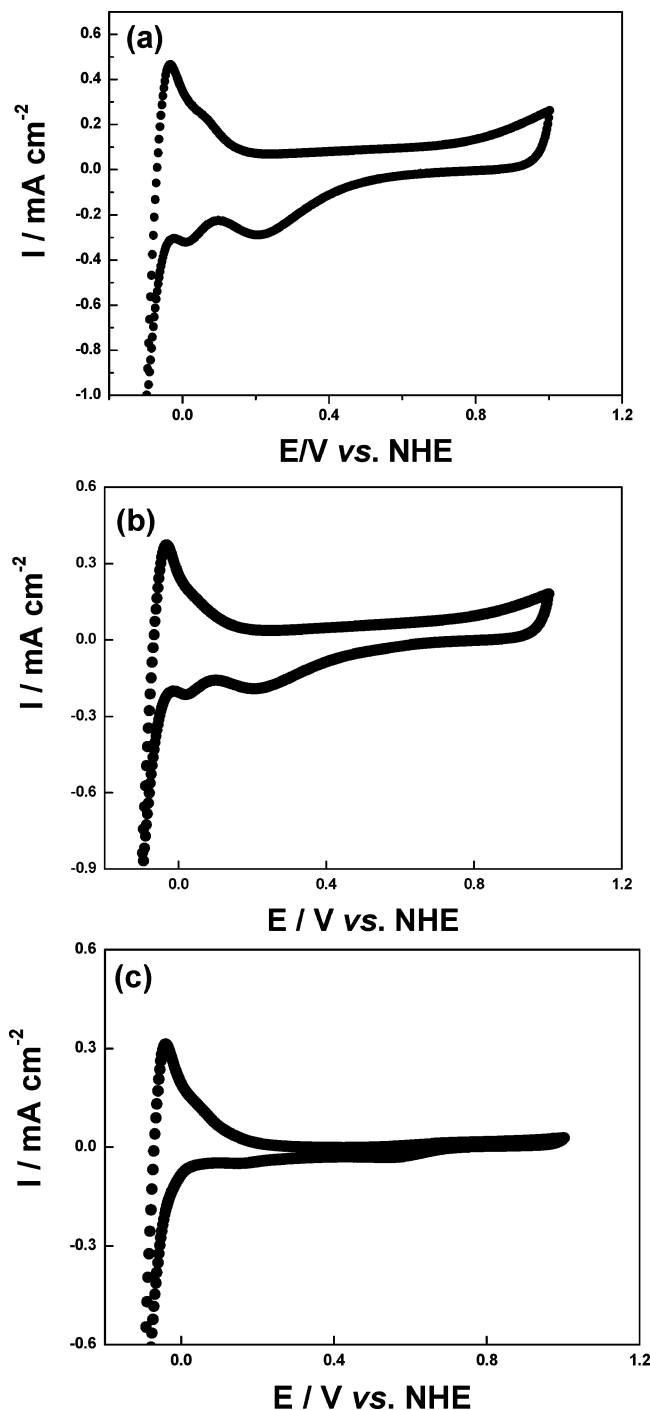


Figure 4. Cyclic voltammograms of Pt layers on metallic dominant Ru thin-film electrodes, as a function of Pt deposition time of (a) 0 s, (b) 10 s, and (c) 2 min, in 0.5 M H₂SO₄ at a scan rate of a 50 mV/s.

Pt layers for 10 s and 2 min compared to that of a Ru electrode without a Pt layer. The metallic dominant Ru electrode without a Pt layer contains XPS characteristic peaks corresponding to Ru chemical states. On the other hand, the XPS spectrum of a Ru electrode deposited by a Pt layer for 10 s (Pt(10 s)/metallic dominant Ru) consists of characteristic peaks corresponding to both Ru and Pt. In addition, the XPS peaks of Pt(10 s)/metallic dominant Ru provide that an atomic ratio of Pt to Ru of the electrode is 60 to 40. In the case of Pt(2 min)/metallic dominant Ru, the XPS spectra have only Pt characteristic peaks without any characteristic peaks corresponding to Ru, which indicates the Pt layer is completely covered on the Ru electrode. Figure 4 shows characteristic curves of metallic dominant Ru electrodes

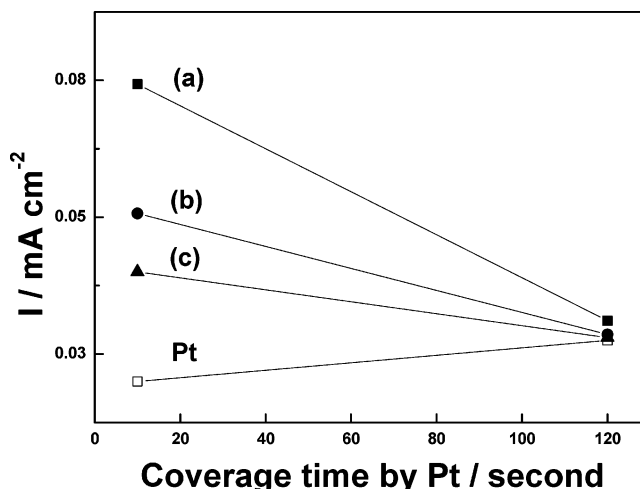


Figure 5. Plot of methanol electrooxidation current density of Pt layers on (a) metallic dominant, (b) mixed, and (c) oxidative Ru thin-film electrodes as a function of a Pt deposition time in 2 M CH₃OH + 0.5 M H₂SO₄ at 0.5 V.

covered by Pt as a function of time in sulfuric acid. The cyclic voltammograms of pure Ru, Pt(10 s)/metallic dominant Ru, and Pt(2 min)/metallic dominant Ru correspond to electrochemical properties of pure Ru, a mixture of Ru and Pt, and pure Pt, respectively. In addition, such CVs of the Figure 4 are in a good agreement with the XPS data of Figure 3. In general, electrochemical characteristic curves are modified as the amount of Ru in the PtRu electrodes was increased. As the Ru component in the electrode becomes dominant, the thickness of the double layer region is increased due to the hydrophilic properties of Ru. Furthermore, considering the catalytic activity for a methanol electrooxidation of PtRu thin-film electrodes, it is well-known that the ≈ 40 –60 at. % of Ru in the PtRu alloy catalysts is optimum for achieving excellent catalytic activity in methanol oxidation.⁹ Accordingly, Pt(10 s)/Ru electrodes with a surface composition of Pt₆₀Ru₄₀ will provide an optimum condition to compare the catalytic activity of methanol electrooxidation in the electrodes. Figure 5 shows a plot of methanol electrooxidation current density of Pt/Ru thin-film electrodes as a function of coverage time by Pt at 0.5 V. It is clear that a catalytic activity of thin-film electrodes deposited by Pt for 10 s is strongly dependent on modified Ru thin-film electrodes, which consist of metallic dominant, mixed, and oxidative Ru states. The order of catalytic activity in methanol electrooxidation is Pt on metallic dominant Ru > Pt on mixed Ru > Pt on oxidative Ru > only Pt. This indicates that Ru metallic and/or oxidative sites with various (electro)chemical states in PtRu electrodes are key sources of oxygen required for removal of CO adsorbed on Pt. However, it is remarkably interesting that a Pt on the metallic Ru electrode has an excellent catalytic activity compared with Pt on mixed or oxidative Ru electrode. Recently, Viswanathan et al. reported from in situ XANES measurement that the active catalytic component is a PtRu alloy with metallic dominant states.³⁶ In addition, we also observed that the PtRuRhNi alloy nanoparticle has a dominant Ru metallic property, which can be attributed to the high activity and the lower deactivation in methanol electrooxidation than those for the conventional PtRu alloy electrocatalyst.⁷ Kim et al. suggested that since an enhancement of methanol electrooxidation by ruthenium is more prominent at low potentials, where metallic ruthenium is present, it could be concluded that the presence of a Ru metallic state is a prerequisite for effective methanol oxidation.³⁷ Accordingly, the Pt on Ru electrode with a dominant Ru metallic property shows improved methanol electrooxidation compared to Pt/Ru

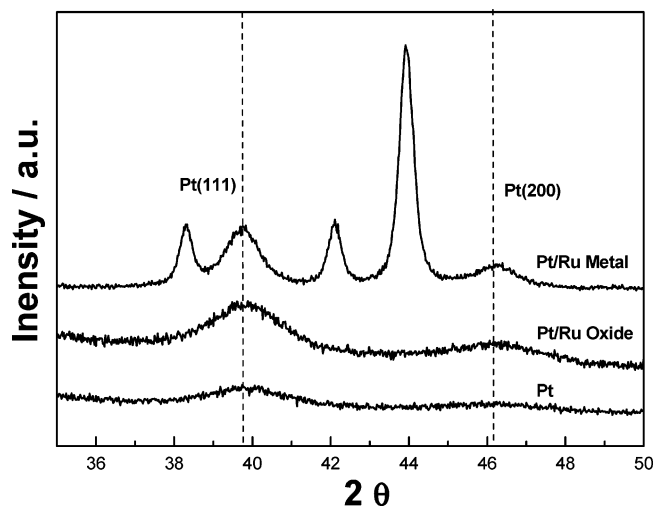


Figure 6. X-ray diffraction patterns of Pt nanosized catalysts on Ru metal and oxide compared with that of the pure Pt nanoparticle. The dotted vertical lines correspond to peaks of Pt polycrystalline face-centered cubic structure.

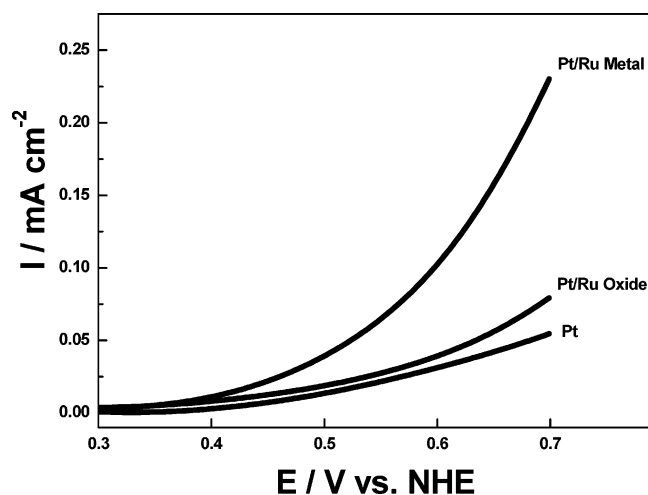


Figure 7. Plot of methanol electrooxidation current density versus accelerating potentials of Pt nanosized catalysts on Ru metal and oxide in 2 M CH_3OH + 0.5 M H_2SO_4 compared with that of pure Pt nanoparticle without Ru states.

electrodes with a mixed or oxidative Ru property. In contrast to Pt(10 s)/Ru electrodes, Pt(2 min)/Ru electrodes show no large difference of catalytic activity for methanol electrooxidation. This indicates that the Pt layer completely covered on the Ru electrode could not affect methanol reaction of Pt by Ru (electro)chemical states. The Pt catalyst electrodes not affected by Ru states show no big difference in methanol oxidation electrocatalysis.

It is significant that such an electrocatalysis on the thin-film electrodes could be applied to actual systems consisting of Pt and Ru particles. Figure 6 shows X-ray diffraction patterns of Pt nanoparticles on the Ru metal or oxide particles prepared by the chemical method.^{38,39} The XRD patterns clearly demonstrate the characteristic peaks of the Pt face-centered cubic structures. In the XRD peak analysis, the average size of the Pt particles is about 3–4 nm, as calculated using the Debye–Scherrer equation, which is in good agreement with that observed by TEM analysis. In addition, as shown in Figure 7, the order of methanol electrooxidation of the nanoparticles is Pt/Ru metal > Pt/Ru oxide > pure Pt nanoparticle in a good agreement with an electrocatalysis of Pt on the Ru thin-film electrodes. It is more important that Ru metallic and/or oxidative sites in PtRu

electrodes are key sources of oxygen required for removal of CO compared to pure Pt without any Ru state. However, the conclusion that any Ru chemical state would be only an absolute prerequisite for an effective methanol oxidation should be considered with extreme caution. In addition, since the issue of the durability of the electrocatalysts is critical, the more intensive study on long-term stability of the fuel cell system needs to be done, and such investigations on the electrodes are currently underway as well.

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