

수소-알코올연료전지를 위한 금속-산화물 나노구조제어

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Control of Metal-Oxide Nanostructures for H₂-Alcohol Fuel Cells

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Abstract : Due to their excellent catalytic activity with respect to methanol oxidation on platinum at low temperature, platinum nanosized catalysts have been a topic of great interest for use in direct methanol fuel cells (DMFCs). Since pure platinum is readily poisoned by CO, a by-product of methanol electrooxidation, and is extremely expensive, a number of efforts to design and characterize Pt-based alloy nanosized catalysts or Pt nanophase-support composites have been attempted in order to reduce or relieve the CO poisoning effect. In this review paper, we summarize these efforts based upon our recent research results. The Pt-based nanocatalysts were designed by chemical synthesis and thin-film technology, and were characterized by a variety of analyses. According to bifunctional mechanism, it was concluded that good alloy formation with 2nd metal (e.g., Ru) as well as the metallic state and optimum portion of Ru element in the anode catalyst contribute to an enhanced catalytic activity for methanol electrooxidation. In addition, we found that the modified electronic properties of platinum in Pt alloy electrodes as well as the surface and bulk structure of Pt alloys with a proper composition could be attributed to a higher catalytic activity for methanol electrooxidation. Proton conducting contribution of nanosized electrocatalysts should also be considered to be excellent in methanol electrooxidation (Spillover effect). Finally, we confirmed the ensemble effect, which combined all above effects, in Pt-based nanocatalysts especially, such as PtRuRhNi and PtRuWO₃, contribute to an enhanced catalytic activity.

1. 서 론

Recently, low-temperature fuel cells such as direct methanol fuel cell (DMFC), which uses methanol directly as the fuel source, has attracted a great deal of interest because of its numerous advantages such as ease of handling a liquid fuel, high energy density and low operating temperatures (even at room temperature).

The electrocatalysis of electrodes in the DMFC represents the oxidation of methanol fuel and the reduction of oxygen, the oxidant. Especially, DMFC performance is dominantly affected by methanol electrooxidation at anode. The general half-reaction for oxidation of methanol is proposed by dual pathway

The oxidation of methanol is associated with an

unknown intermediate in the oxidation of CO₂ spontaneously and CO_{ads} as a poison to require the additional reaction by 2nd elemental metal for the dehydrogenation reaction. According to Langmuir

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Hinshelwood mechanism, CO_{ads} on Pt is oxidized into CO_2 recombining with oxygen species on, especially, Ru. The Ru surface atoms provide nucleation sites for the adsorption of oxygen-containing species, which can initiate the further electrooxidation of CO adsorbed either on a Pt site nearby, the so called *bifunctional effect*.

An important issue in the interaction between Pt and molecules is the chemisorption of carbon monoxide (CO), a by-product of methanol electrooxidation, on the Pt electrode. Typically, the CO-metal bond is described in terms of electron donation from the CO 5 to the metal and back donation from the metal to the CO 2*. Two important effects operate. First, the 5 contribution to the bonding is quite small. There are few antibonding states shifted above the Fermi level. This is true for Au. The large difference from the 5 case is that 2state is above the Fermi level before interaction with the d states, and in this case new bonding states are shifted below the Fermi level. In the case of noble metals, 2-metal d interactions are dominant. In addition, in the case of the left in the Periodic Table from the noble metals, the bond strength increases because the d states move up in energy. Accordingly, the modification of d electronic properties of catalyst, the so called *electronic effect (or ligand effect)*, would lower the density of state (DOS) on the Fermi level and reduce the bond energy between catalyst and CO, thus enhancing catalytic methanol oxidation activity.

Except for the Langmuir-Hinshelwood mechanism and electronic effect, many effects for increasing the activity of methanol electrooxidation have been studied. In particular, the transfer of a proton to the support surface, especially, of tungsten oxide, during the oxidation of fuels such as methanol or hydrogen would create clean active sites on the platinum, and thus continue the efficient dehydrogenation of the catalyst, the so called *hydrogen spillover effect*.

Finally, the synergy, the so called *ensemble effect*, combined bifunctional, electronic, and spillover effect via 2nd, 3rd, or 4th elements, could be expected in catalytic reaction. In particular, based on the electrocatalysis mechanism and structure consideration, novel nanostructured electrocatalysts have been extensively studied and designed by means of chemical synthesis or physical method.

2. 실험방법

Chemical synthesis for nanocatalysts

A variety of methods can be used for the preparation of a Pt alloy catalysts. Chemical methods can be classified into impregnation and colloidal methods. In the impregnation method, alloys are prepared from metal salts using reducing agents or by reductive annealing. In

the colloidal method, Watanabe *et al.* formed platinum oxides and ruthenium oxides in aqueous media, followed by reductive annealing under a stream of hydrogen gas. Bönnemann *et al.* prepared surfactant-stabilized PtRu alloy clusters, $[\text{PtRu-N}(\text{Oct})_4\text{Cl}]$ in nonaqueous media, the particle size of which was less than 2 nm and in which the particle size distribution was well-defined. Götz *et al.* and Schmidt *et al.* applied this method to fuel cells and added heat treatment procedures to remove the surfactant and to increase the catalytic activity. In addition, we found that Pt nanoparticles with 1.7 nm in size were formed by using a modified colloid method in an anhydrous atmosphere [29,30].

Physical deposition method for nanocatalysts

In general, another approach to catalysis study by means of thin-film technology, e.g., evaporation and sputtering method, can understand the anode/cathode catalysis and mechanism.

Structural analysis of nanocatalysts

To analyze structure of the Pt nanoparticles, the X-ray diffraction (XRD) method was carried out. From the obtained XRD patterns of nanocatalysts, the size and/or composition were obtained using the Debye-Scherrer equation and Vegard's law. Similar to typical XRD diffraction, grazing incidence X-ray diffraction (GIXRD) measurements were conducted for composition and phase behavior of thin-film electrode catalysts. For size and distribution of nanocatalysts, the transmission electron microscopic (TEM) investigation was carried out.

Chemical analysis of nanocatalysts

The surface coverage and chemical states on the electrocatalysts were determined by X-ray photoelectron spectroscopy (XPS). In addition, chemical and electronic states in the nanocatalysts were confirmed by X-ray absorption near edge (XANES) spectra. Rutherford backscattering spectroscopy (RBS) was used to determine the composition of the alloy thin-film electrodes.

Electrochemical analysis of nanocatalysts

Electrochemical measurements were conducted using a three-electrode cell at 25 °C. A Pt gauze and an Ag/AgCl (in saturated KCl) were used as the counter and reference electrodes, respectively. The working carbon electrode (6 mm in diameter) was polished with 1, 0.3, and 0.05 m Al_2O_3 paste and washed ultrasonically in Millipore water (18 M Ω cm). The catalyst ink, consisting of the catalyst and the Nafion ionomer in water and 2-propanol was dropped on the working electrode, and dried at 70 °C in a vacuum oven. Solutions of 0.5 M H_2SO_4 and 2.0 M CH_3OH in 0.5 M H_2SO_4 were stirred constantly and purged with nitrogen gas. All chemicals

used were of analytical grade. Electrochemical experiments were performed using an AUTOLAB instrument from Eco Chemie. In order to compare the catalytic activity of the supported catalysts with respect to methanol oxidation, voltammetry was performed in the potential range of 0 ~ 0.7 V vs NHE.

3 결과 및 토의

Nanocatalysts via bifunctional effect

In particular, according to 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. 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. 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. 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. Due to the contribution of RuO_xH_y to proton and electron conducting, a mixed-phase nanosized electrocatalyst containing Pt metal and RuO_xH_y may have considerable potential for use in methanol electrooxidation.

Nanocatalysts via electronic effect

According to the bifunctional mechanism, anode catalysts in DMFCs have been studied the most intensively. The CO poisoned platinum can be regenerated via the reaction of surface CO with oxygen species associated with elements such as ruthenium and osmium to yield CO₂. Smotkin *et al.* reported on improved methanol electrooxidation catalysts such as PtRu, PtOs and PtRuOs and confirmed the role of ruthenium and osmium as oxygen sources, consistent with the bifunctional mechanism. Goodenough *et al.* reported a shift in the Pt4f peak of a Pt/Ru alloy using XPS analysis, showing that some electronic effects can also be involved in ruthenium enhancement. In addition, the electronic properties of Pt/Ni, Pt/Co, and Pt/Fe thin-film electrodes have been confirmed by a *d*-vacancy shift in XPS. In particular, we found that Pt/Ni and Pt/Ru/Ni nanoparticles showed a shift in the Pt4f peak in a Pt/Ni-based alloy structure, so called the electronic

effect. Enhanced catalytic activity such as lower on-set potential and improved stability in methanol electrooxidation was responsible for the change in the electronic properties of Pt in Pt/Ni alloys.

Nanocatalysts via spillover effect

Because of the current interest in fuel cells that operate at relatively low temperatures (< 80 °C), catalytic reactions such as the oxidation of fuels at the anode or the reduction of oxygen at the cathode have been a subject of considerable interest. The transfer of hydrogen to the support surface during the oxidation of fuels would require platinum as the clean active site to achieve the efficient dehydrogenation of the catalyst, this phenomenon, the so called hydrogen spillover effect. In particular, Rolison *et al.* suggested that hydrous ruthenium oxides (RuO_xH_y) played an important role in mediating proton transporting during methanol electrooxidation. Due to proton conducting contribution of RuO_xH_y, mixed-phase nanosized electrocatalyst containing Pt metal and RuO_xH_y may be considered to be excellent in methanol electrooxidation. Similar to Pt-RuO_xH_y, we reported the enhanced catalytic activity in the Pt-WO₃ consisting of Pt nanometallic phase and WO₃. This means that proton conducting oxides such as RuO_xH_y and WO₃ may play a key role for the enhanced methanol electrooxidation. Here we describe a Pt-WO₃ and Pt-RuO₂ nanophase electrodes, prepared by asputtering process that is similar in structure to a bulk nanoparticle catalyst electrode and the direct observation of hydrogen transfer from platinum to the substrate using electrochromism in the tungsten or ruthenium oxide [40]. The Pt-WO₃ nanophase electrode showed much more enhanced electrocatalytic activity than a Pt itself for methanol oxidation and exactly the reverse change in optical signal intensity with respect to electrochemical cell potential, compared with an electrochromic WO₃ electrode, suggesting the hydrogen spillover from Pt to WO₃. Consequently, it was possible to directly observe the in situ hydrogen transfer from platinum to tungsten oxide in a fuel cell electrode using electrochromism. The transfer of hydrogen ions, produced on the platinum during the electrooxidation of methanol, to the tungsten oxide could ensure clean active reaction sites on the platinum thus enhancing the electrooxidation current density. The relationship between the electrical and hydrogen transport properties of ruthenium oxide and its electrode performance with respect to methanol electrooxidation was investigated using a Pt-RuO₂ nanocomposite thin-film electrode fabricated by means of a co-sputtering system. The performance of the nanocomposite electrode, consisting of a Pt nanophase and a RuO₂, was modified by heat treatment at different temperatures which altered the proton and electron contribution in the electrodes. In addition, recently, we

reported that enhanced proton transport and catalyst activity of the electrodes with Ta₂O₅ or TiO₂ similar to contribution of WO₃ or RuO₂ in the electrocatalysts.

Nanocatalysts via ensemble effect

The excellent catalytic activity of platinum with respect to methanol oxidation at low temperatures makes this metal electrocatalyst ideal for use as an anode. However, since the pure platinum is readily poisoned by CO species, a by-product produced during methanol oxidation, considerable effort has been made to design and synthesize Pt-based alloy catalysts by alloying platinum with other elements in order to enhance its catalytic activity by eliminating or inhibiting the CO poisoning effect. An important process to overcome CO poisoning effect and improve methanol oxidation is as follows (bifunctional effect): the CO-poisoned platinum can be freshened by means of the reaction of surface CO with oxygen species adsorbed on a water activating element such as ruthenium to oxidize CO into CO₂. In addition, it has been reported that enhanced methanol oxidation in Pt-based nanoparticles, which have been alloyed with a transition metal such as Ni, which has a lower electronegativity than Pt, can be attributed to a change in the electronic properties of Pt (electronic effect). Accordingly, to confirm ensemble effect combined bifunctional, electronic, and spillover effect via 2nd and 3rd or 4th elements, the catalytic activity of PtRuRhNi was examined in relation to the oxidation of methanol in a direct methanol fuel cell. As evidenced by transmission electron microscopy analysis, the synthesized PtRuRhNi appeared to be a well-synthesized Pt-based alloy nanoparticle. Through XANES and XPS, it was found that Pt and Ru in the PtRuRhNi are present in electronic and chemical states that are favorable to methanol electrooxidation. The dominant existence of Pt and Ru metallic states on the catalyst was essential for its high surface activity with respect to methanol electrooxidation. However, the catalytic enhancement of PtRuRhNi due to the chemical states of Rh/Ni was considered and examined. PtRu-WO₃ nanocomposite electrodes, for methanol electrooxidation as an example of Pt-based nanocatalysts via ensemble effect were fabricated by means of a sputtering method. The homogeneous dispersion of alloy catalyst and well-formed nanophase structure in the PtRu-WO₃ would lead to an excellent catalytic electrode.

4. 결론

In the low-temperature fuel cell, since Pt is readily poisoned by CO, a by-product of methanol electrooxidation, and is extremely expensive, a number of efforts to design and characterize Pt-based

nanocatalysts have been attempted. In particular, the Pt-based nanocatalysts were designed by both chemical synthesis and physical method such as thin-film technology. Using the nanoparticles and nanocomposite or thin-film type catalysts, bifunctional, electronic, spillover, ensemble effects for enhanced methanol electrooxidation were investigated. Simultaneously, based on these mechanisms, high-performance nanostructured electrocatalysts could be prepared. The design rule of electrocatalysts, i.e. nanocatalysts via both electrocatalysis mechanism and various preparation methods will be applied to hydrogen fuel cell electrodes as well as DMFC cathode.

후기

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