Fabrication of Pt–Re atomic alloy catalysts by alloying of atomically dispersed Pt with Re inside the β -zeolite pores for an oxygen reduction reaction

LINSHENG WANG^{1,2,3,*} and LICHENG LIU^{3,4}

¹National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan

²National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8585, Japan

³The University of Electro-Communications, Tokyo 182-8585, Japan

⁴Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, People's Republic of China

*Author for correspondence (linsheng_wang@yahoo.com; WANG.Linsheng@aist.go.jp)

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Abstract. The Pt–Re atomic alloy is fabricated by alloying of atomically dispersed Pt with Re inside the β -zeolite pores with a size of 0.5–0.6 nanometres. The atomically dispersed Pt–Re alloy species exhibit a surprisingly high mass activity of about 60 A g_{Pt}^{−1} for the oxygen reduction reaction, which is much higher than that of the existing Pt nanoparticle catalysts with a Pt particle size of several nanometres.

Keywords. Pt–Re atomic alloy catalyst; super-high mass activity; oxygen reduction reaction; alloying of atomically dispersed Pt with Re; β -zeolite pores.

1. Introduction

Polymer electrolyte membrane fuel cells (PEFCs) have become one of the best power sources to realize green and efficient energy generation for many commercial applications. Platinum (Pt) metal particles with a particle size of several nanometres have been the most efficient catalyst for an efficient oxygen reduction reaction (ORR) in PEFCs, in addition to their high stability under strong PEFC acidic conditions [1,2]. However, the cost of Pt is very high and resources of Pt are very limited. This has led to a slowdown of the global commercialization process of PEFCs [1,3,4]. The use of a minimal amount of Pt in the electro-catalyst by maximizing the mass activity of Pt in the electro-catalyst has been a widely accepted solution to reduce the cost of PEFCs. The enhancement of the mass activity of Pt by adding a second inexpensive metal to Pt to form either a Pt core–shell [5–8] or a Pt alloy in order to increase the surface area of Pt per unit amount [9–12] has been extensively studied as a major strategy. The enhancement of Pt mass activity by reducing the particle size of Pt in order to increase the surface area of the Pt nanoparticles is another promising strategy, which is effective in increasing the mass activity of Pt [13–15]. Minimizing the amount of Pt-ions fed into the Pt reduction process in order to regulate the growth of the nanoparticles can lead to a decrease of the size of Pt nanoparticles. We had previously fabricated Pt and Pt–Re clusters in the pores of ZSM-5 zeolites and Pt, Ir and Ni clusters in the pores of β -zeolites,

which were utilized for solving the highly difficult selective oxidation reactions [16,17]. In the present study, atomically dispersed Pt alloyed with Re is fabricated inside the pores of β -zeolite and characterized by scanning transmission electron microscopy (STEM), X-ray diffraction (XRD) and TG-DTA. The catalytic activity of the fabricated Pt–Re alloy species inside the sub-nanospace for the ORR is studied.

2. Experimental

Zeolite β with a SiO₂/Al₂O₃ ratio of 25 was purchased from Zeolyst International. Pt species were introduced into the pores of the β -zeolite by a repeat ion-exchange method to obtain a Pt/ β sample. The measured BET surface area of the Pt/ β sample is about 550 m² g^{−1} by using N₂ adsorption. STEM images were obtained on a JEOL JEM-2010 and JEM-2100F at an accelerating voltage of 200 kV. XRD patterns were recorded by using a Rigaku Ultima III diffractometer with Cu K α radiation (λ = 0.154178) at 40 kV and 40 mA. The scanning angle (2θ) ranged from 5 to 50° at a scanning rate of 5° min^{−1}. Electrochemical experimental measurements for cyclic voltammogram (CV) and rotating disk electrode (RDE) measurements were performed using an Autolab potentiostat/galvanostat in a standard three-electrode configuration with a reversible hydrogen electrode (RHE) as the reference electrode and a Pt foil as the counter electrode at room temperature. A glassy carbon (GC) disk electrode (from

Figure 1. STEM images of Pt(0.25 wt%)/ β sample after calcination, yellow lines are typical pore wall lattices and black arrows indicate typical Pt clusters.

PINE instruments) was polished with alumina with a particle size of about 0.05 μm before electrochemical experimental measurements and it was used as a working electrode. The thin film catalyst layer on the GC electrode was prepared by using 12.5 mg catalyst, 18 ml Millipore water and 2 ml Nafion solution (0.5 wt%) ultra-sonicated for 20 min to obtain a well-dispersed catalyst ink. The catalyst ink of about 20 μl was then quantitatively put on the GC electrode by using a micropipette and dried in a vacuum to obtain a catalyst thin film. The CVs were recorded between the potentials of 0.05 and 1.2 V vs. RHE at a sweep rate of 50 mV s^{-1} and under continuous flowing pure nitrogen purging. The ORR activity was examined by linear sweep voltammetry (LSV) by scanning from 0.3 to 1.0 V vs. RHE in the anodic potential sweep direction and at a scan rate of 10 mV s^{-1} in the electrolyte solution saturated with a flow of pure oxygen by using a MSR rotator from PINE instruments at a rotation speed of 1600 rpm vs. RHE as the reference electrode at a sweep rate of 50 mV s^{-1} .

3. Results

The fabricated Pt/ β samples with a Pt loading of 0.25 wt% were observed by high resolution STEM. The STEM image of the Pt(0.25 wt%)/ β sample is shown in figure 1. The channel wall crystal of the zeolite pores can be clearly seen in the STEM images and the light dots with an average size of about 0.2 nm inside the pores of zeolite can also be found as shown in figure 1.

The light dots inside the zeolite pore represent the Pt metal species with almost atomic dispersion. This indicates that the highly dispersed Pt metal species at almost single atom level is successfully fabricated inside the pores of β -zeolite.

With an increase of Pt loading from 0.25 to 2.1 wt%, the nano-sized Pt particles outside the zeolite pores appear in STEM images. Atomically dispersed Pt is thermodynamically unstable; it is difficult to avoid growing larger to become Pt clusters or Pt particles when they are heated at higher temperatures. Therefore, only the atomically dispersed Pt species inside the zeolite pore can be observed on the calcined Pt(0.25 wt%)/ β sample. Pt species on the calcined Pt(0.25 wt%)/ β sample was also checked by XRD. Figure 2 shows the XRD patterns of the $\text{NH}_4\beta$ sample, Pt(0.25 wt%)/ β samples before and after calcination and Pt(0.25 wt%)-Re (0.3 wt%)/ β sample after calcination. We can see from figure 2 that a small XRD peak at a 2θ angle of about 40 appears on the Pt(0.25 wt%)/ β sample after calcination although the XRD peak is so small. The appearance of the small XRD peak at the 2θ angle of about 40 indicates that the Pt species are partially atomically dispersed inside the zeolite pores and partially exist in the form of small Pt clusters.

The small XRD peak at the 2θ angle of about 40 is ascribed to the small clusters since this peak does not appear on the $\text{NH}_4\beta$ sample and Pt(0.25 wt%)/ β sample before calcination. In order to avoid growing of Pt species from the atomically dispersed Pt to Pt clusters, the Pt(0.25 wt%)-Re (0.3 wt%)/ β sample is fabricated by addition of Re(0.3 wt%) to the Pt(0.25 wt%)/ β sample. Figure 2 shows that no XRD peak appears at the 2θ value of about 40 degree on the Pt(0.25 wt%)-Re (0.3 wt%)/ β samples even after calcination in air at 773 K for 4 h. It is of significance that the atomically dispersed Pt is stable on the Pt(0.25 wt%)-Re (0.3 wt%)/ β sample even after calcination in air at 773 K for 4 h. The stabilizing effect of Re on atomically dispersed Pt is contributed to the alloying effect of Pt atom with rhenium inside the pore of the β -zeolite. The thermo-stability of highly dispersed bimetallic Pt-Re species is higher than that of the monometallic Pt species inside the zeolite pores. The transformation of Pt from the states of oxides to the Pt atoms at zero state valency is accompanied by the heat effect and sample weight loss. The alloying effect of Pt with Re leads to an exothermic heat effect. The TG-DTA profiles of $\text{NH}_4\beta$, Pt (0.25 wt%)/ β and Pt(0.25 wt%)-Re (0.3 wt%)/ β samples under air stream with increasing temperature from room temperature to 773 K are shown in figure 3.

The heat effect and weight change during the calcination process of the as-synthesized Pt(0.25 wt%)/ β and the as-synthesized Pt(0.25 wt%)-Re (0.3 wt%)/ β samples are compared in the TG-DTA experiments. It almost has no evidence of heat effect and weight change on the TG-DTA profiles of $\text{NH}_4\beta$ sample as shown in figure 3. By comparing the TG-DTA profiles of the as-synthesized Pt(0.25 wt%)/ β and Pt(0.25 wt%)-Re (0.3 wt%)/ β with that of $\text{NH}_4\beta$, an evident exothermic heat effect and weight loss occurred at the temperature ranging from 330 to 380°C in the TG-DTA profiles of the as-synthesized Pt(0.25 wt%)/ β and the as-synthesized Pt (0.25 wt%)-Re(0.3 wt%)/ β samples, as shown in figure 3. The exothermic heat effect and weight loss are

Figure 2. XRD patterns of Pt and Pt-Re species fabricated in the pores of β zeolite, (A) $\text{NH}_4\beta$; (B) $\text{Pt}(0.25 \text{ wt}\%)/\beta$ calcined and (C) $\text{Pt}(0.25 \text{ wt}\%)\text{-Re}(0.3 \text{ wt}\%)/\beta$ calcined.

ascribed to the reduction of Pt oxides to Pt atoms. In addition, a much more strong heat effect can be seen on the TG-DTA profile of $\text{Pt}(0.25 \text{ wt}\%)\text{-Re}(0.3 \text{ wt}\%)/\beta$ than that on $\text{Pt}(0.25 \text{ wt}\%)/\beta$, which means that there exists a stronger exothermic heat effect on $\text{Pt}(0.25 \text{ wt}\%)\text{-Re}(0.3 \text{ wt}\%)/\beta$ including the contribution from the alloying effect of Pt with Re to form the Pt-Re atomic alloy species than that during the formation process of single Pt atom species. Since the alloying of atomically dispersed Pt with Re to form the Pt-Re atomic alloy species contributed to the additional exothermic heat effect of the novel Pt-Re atomic alloy species are thermodynamically more stable than the single Pt atom species inside the zeolite pores. The thermodynamic stability enhancement of the atomically dispersed Pt by alloying with Re inside the β -zeolite is important for enhancing its durability in catalytic reactions.

Figure 3. TG-DTA profiles of $\text{NH}_4\beta$, as-synthesized $\text{Pt}(0.25 \text{ wt}\%)/\beta$ and as-synthesized $\text{Pt}(0.25 \text{ wt}\%)\text{-Re}(0.3 \text{ wt}\%)/\beta$ samples.

The atomically dispersed Pt inside the zeolite pore stabilized by alloying with Re as a novel catalyst system is expected to catalyse various reactions. It is well known that Pt nanoparticles supported on active carbons as the catalysts for the ORR in PEFCs have been extensively studied. Here the electrocatalytic activity of the novel Pt-Re atomic alloy catalyst for the ORR is studied, and we hope that it may open a door for developing more efficient and durable electro-catalysts for PEFCs using a minimal amount of Pt. The CV of the $\text{Pt}(0.25 \text{ wt}\%)\text{-Re}(0.3 \text{ wt}\%)/\beta$ catalyst is tested and the CV profile is shown in figure 4 for a comparison with that of the traditional Pt/C catalysts. The CV profile was recorded at a scan speed of 50 mV s^{-1} in 0.1 M HClO_4 solution.

There are about 3 peaks appearing in the CV profile in figure 4. The peak in the potential region of $0.12\text{--}0.28 \text{ V}$ is assigned to the H_2 adsorption/desorption. The peak in the potential region of $0.4\text{--}0.8 \text{ V}$ is assigned to the double-layer charging and the peak in the potential region of $0.8\text{--}1.2 \text{ V}$ is assigned to the $\text{OH}(\text{ad})/\text{O}(\text{ad})$ formation/reduction respectively. The shape of CV curve in the H_2 adsorption/desorption region (at about 0.2 V) and the electric double layers (at about 0.6 V) were wide for the catalyst. Cathodic reduction of the oxygenated species on the surface was also identified, which indicate that abundant oxygenate species can be formed on the surface layer of the catalyst. The basic CV features of the novel $\text{Pt}(0.25 \text{ wt}\%)\text{-Re}(0.3 \text{ wt}\%)/\beta$ catalyst with highly

Figure 4. CV for the Pt(0.25 wt%)-Re (0.3 wt%)/ β catalyst recorded at a scan speed of 50 mV s^{-1} in 0.1 M HClO_4 solution.

Figure 5. O_2 reduction polarization curves for the Pt (0.25%)-Re (0.3%) sample with varying rotation rates from 100 to 1600 rpm by RDE measurements.

dispersed Pt-Re atomic alloy species inside the zeolite pores are similar to that of the traditional Pt/C based nanoparticle electro-catalysts with the Pt particle sizes of several nanometres. The fabricated novel materials of Pt-Re atomic alloy active species were used as a novel electro-catalyst for electro-catalytic reactions. The mass activity of the fabricated Pt-Re atomic alloy species inside the zeolite pores as the novel catalyst for the ORR was tested by the RDE measurement method. Figure 5 shows the RDE measurement results for the ORR on the Pt (0.25%)-Re (0.3%)/ β catalyst placed on a GC electrode in oxygenated 0.1 M HClO_4 solution at room temperature for various rotation rates. This shows O_2 reduction polarization curves for the Pt (0.25%)-Re (0.3%)/ β catalyst with varying rotation rates from 100 to 1600 rpm by RDE measurements (about 2 μg sample was used).

Figure 6. The mass activity calculated from the LSV experiments by using the Koutecky-Levich equation, $1/j_k = 3300000$; $j_k = 0.0003 \text{ mA}$ (at 0.9 V).

It is clear from figure 5 that the O_2 reduction polarization curves for the Pt (0.25%)-Re (0.3%)/ β catalyst are evidently varying with varying rotation rates from 100 to 1600 rpm by RDE measurements although the amount of Pt contained in the catalyst layer placed on the RDE is only about $0.0255 \mu\text{g cm}^{-2}$. The experimental results in figure 5 demonstrate the mixed kinetic/diffusion control region of the ORR on the novel Pt (0.25%)-Re (0.3%)/ β catalyst and the Pt-Re atomic alloy species inside the pores are highly efficient for catalysing the ORR. The Koutecky-Levich plots obtained from figure 5 at 0.9 V are shown in figure 6.

The linearity of this plot shown in figure 6 is a sign of first-order kinetics with respect to molecular oxygen [18]. Using the Koutecky-Levich equation:

$$1/j = (1/j_k + 1/j_D) = (1/nFkc_{\text{O}_2} + 1/B\omega^{1/2}) \quad (1)$$

where j is the measured disk current density, j_k is the kinetic current density, j_D is the diffusion current density, F is the Faraday constant, k is the reaction rate constant, c_{O_2} is the concentration of dissolved O_2 , B is a constant and ω is the rotation rate, one can calculate the kinetic currents of O_2 reduction from the intercepts of the $1/j$ axis at $1/\omega^{1/2} = 0$. The mass activity (MA) of the electro-catalyst was calculated from the LSV experiments as depicted in figure 5 by using the following Koutecky-Levich equation (neglecting the Nafion film-diffusion-limited current). The ORR polarization curve was measured at varying rotation speeds (figure 5). The Koutecky-Levich plots for O_2 reduction were then generated in a range of potentials (figure 6), showing that curves are linear over the potential. These plots use the principle of the limiting current (i_l), as described in equation (1). The intercept of the Koutecky-Levich plot is the inverse of the kinetic current ($1/i_k$), while the slope is $1/B$. The j_k value obtained in figure 6 is 0.0003 mA at a potential of 0.9 V. The MA normalized to the metal amount for the ORR on

Pt(0.25 wt%)-Re (0.3 wt%)/ β as the novel electro-catalyst is about $60 \text{ A g}_{\text{Pt}}^{-1}$ according to the following calculation, where MA is expressed as normalized kinetic current (i_k) at a potential of 0.9 V.

$$\begin{aligned}\text{MA} &= j_k / (\text{catalyst weight} \times \text{Pt loading}) \\ &= 0.0003 \text{ mA} / (2 \mu\text{g} \times 0.25\%) = 60 \text{ A g}_{\text{Pt}}^{-1}.\end{aligned}$$

The mass activity of the novel Pt(0.25%)-Re (0.3%)/ β electro-catalyst is much higher than that of the traditional Pt/C-based catalysts.

4. Conclusions

Fabricated atomically dispersed monometallic Pt inside the β -zeolite pores is thermodynamically unstable and partially transformed to Pt clusters after calcination under air stream at 773 K. The atomically dispersed Pt is thermodynamically stabilized by alloying with Re and it exists homogeneously inside the zeolite pores even after calcination in air stream at 773 K. The atomically dispersed Pt-Re atomic alloy as a novel catalyst system exhibits a high MA of about $60 \text{ A g}_{\text{Pt}}^{-1}$ for the ORR, which opens a door for developing highly efficient electro-catalysts for ORRs in PEFCs.

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