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Quaternary Pt-based electrocatalyst for methanol oxidation by combinatorial electrochemistry

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Abstract

The demonstration to apply the combinatorial method using a repeated cyclic voltammetry is reported to find the anodic material for DMFC that shows a higher electrocatalytic activity and that can replace a portion of precious metals with cheap ones. The activity of newly found electrocatalyst whose composition was determined through high-throughput screening was compared with that of commercially available Johnson–Matthey Pt(50)Ru(50). It was found Pt(77)Ru(17)Mo(4)W(2) was more active and stable than Pt(50)Ru(50) in methanol electro-oxidation. The repeated cyclic voltammetry makes the combinatorial method expand into a screening tool to find the electrocatalyst that not only showing an initial excellent performance but also being active in the long-run reaction. © 2002 Published by Elsevier Science B.V.

Keywords: High-throughput screening; Methanol oxidation; Direct-methanol fuel cell; Electrocatalyst

1. Introduction

Combinatorial chemistry and high-throughput screening have had an enormous impact on the drug discovery in the pharmaceutical industry and are complementary technologies for the preparation of large numbers of formulations and their performance testing [1–3]. Electrocatalyst is an attractive inorganic material for combinatorial exploration.

Direct-methanol fuel cell (DMFC) is one of the most interesting power sources of clean energy and is expected to be used as a portable power source. However, the main drawbacks limiting the practical realization of DMFC are the high overpotential at the anode catalyst combined with the necessity of operating at low temperatures, the poisoning arising from carbonyl group-containing intermediate compounds adsorbed on anode, and the high cost for preparing the precious metal electrode [4–6]. In order to solve these problems, considerable efforts have made in search of DMFC anode catalyst, especially for methanol electro-oxidation [7–11]. Despite nearly three decades of research and optimization, one of the best known anode material is Pt(50)Ru(50) (numbers in parentheses are in atomic percent) alloy [12–16]. Consequently, there exists a need for methods providing the rapid assessment of many anode electrocatalysts of which compositions are all different and the combinatorial method is being developed rapidly into an attractive solution. Recently, the combinatorial electrochemistry applied to discover the new catalyst for methanol electro-oxidation has been reported using an optical detection by a fluorescent acid–base indicator [17] or the automated multi-electrode

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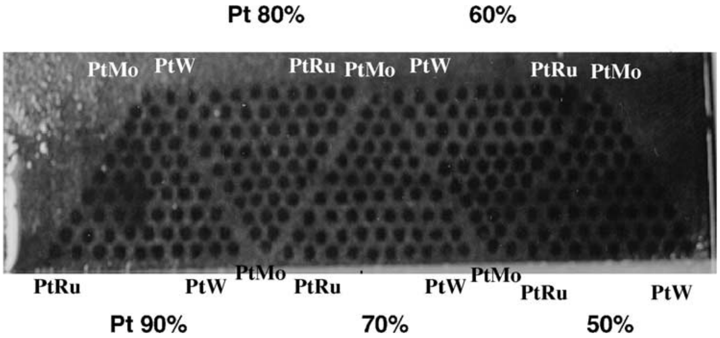

Fig. 1. Combinatorial optical image before screening.

arrays [18]. Now we report the demonstration to apply the former technique to find the anodic material that shows a higher and more stable electrocatalytic activity. For this purpose, we conducted the high-throughput screening after the repeated cyclic voltammetry.

Since CO_{ads} is postulated to be an intermediate in methanol electro-oxidation on Pt alloy surfaces and to decrease the number of active sites, it is very important to oxidize CO adsorbed on Pt to CO_2 to enhance the electrocatalytic activity of Pt. More active and stable catalyst can reduce the amount of the noble metal used in DMFC. Especially, we focused on the elements, W and Mo, which to us seemed to be the most promising candidates to reduce the ruthenium content of Pt(50)Ru(50), because it is supposed that tungsten and molybdenum are active as a redox catalyst [19,20].

On this point of view, it is believed that optimization of the composition of the Pt-based electrocatalyst containing non-noble metals, W and Mo, via combinatorial electrochemistry is clearly crucial to commercializing DMFC.

2. Experimental

By analogy with the reported procedure [17], the ink-jet printer (Samsung Myjet Plus) was calibrated by UV–VIS spectroscopy (HP89500) by printing the amount of each precursor onto polyester film and then perfectly desorbing each spot into a known volume of water. And we prepared the adjusted mole concentrations of $H_2PtCl_6 \cdot xH_2O$, $RuCl_3$, $(NH_4)_6W_{12}O_{39} \cdot xH_2O$, and $MoCl_5$ (Aldrich) and controlled the drawing software to print the metal–salt ink on Toray carbon paper. The prepared array shown in Fig. 1 contains 275 (55 × 5) different compositions of which total moles of metal are identical and 0.19 μmol per spot and is composed of five groups. Its vertices of each group are PtRu, PtMo, and PtW and edges are 24 ternary compositions. The face consists of 28 quaternary arrays. The mole percent of Pt of each group is 90, 80, 70, 60, and 50%. The reduction procedure was carried out by placing the array into a glass cell containing 0.2 M $NaBH_4$ solution adjusted to pH 8 at 70 °C for 5 h. And then it was removed from the cell and thoroughly washed with ultrapure water and dried for overnight at 110 °C.

The electrolyte solution was composed of 100 μM quinine as a proton indicator, 6 M of reactant methanol, and the diluted H_2SO_4 which was added to adjusted pH to 7. The potential-step experiments were carried out using a potentiostat/galvanostat controlled by an IBM PC. Especially, because our experiments were focused on the oxidation of CO adsorbed on Pt active sites, the combinatorial screening was conducted after 20 times of cyclic voltammetry. Each spot was used as a working electrode. Cyclic voltammetry experiments were conducted between 0.075 and 0.5 V vs. RHE at the sweep rate of 20 mV/s. The most active working electrode was selected by the brightest spot of the array obtained by fluorescence emission excited by UV of 254 nm. The quantity of Pt-based catalyst whose composition was determined through combinatorial screening was prepared and further studied at room temperature by stationary current–voltage curves and chronoamperometry in a three-electrode cell.

In order to prepare the catalyst-modified thin film electrode, catalysts were dispersed ultrasonically in water in a concentration of 4 mg/ml and a 20 μl aliquot was transferred onto a glassy carbon substrate. After evaporating water, the resulting thin catalyst film was covered with 20 μl of a Nafion solution.

The bulk composition of the catalyst materials was investigated by EDX or ICP. The geometric surface areas of the catalysts were determined by the BET method using nitrogen as the adsorbate and the average particle size was also estimated from XRD result.

3. Results and discussion

Watanabe et al. [12] first demonstrated the well-controlled PtRu alloy clusters prepared by the co-deposition of fine Pt and Ru oxides and reduction with H_2 bubbling and discussed the bi-functional mechanism. And they concluded that the catalytic activity originated not from the bulk composition but from the surface composition exclusively. And Gasteiger et al. [6,14,21] reported at least three adjacent Pt sites were needed for methanol chemisorption, suggesting a surface Pt/Ru ratio greater than unity. It was shown that the alloy with a surface of ≈10 at.% Ru exhibited the highest catalytic activity toward the electro-oxidation of methanol (0.005–0.5 M) at 25 °C and 0.5 V. In contrast, it was found that the optimal surface composition for electro-oxidation of CO was 1:1 [22] and that an alloy with a Ru surface composition of ≈50 at.% exhibited the highest activity, with approximate reduction of the oxidation potential of 0.025 V compared to pure Pt and 0.1 V compared to Ru. Chu and Gilman [16] also evaluated methanol electro-oxidation activity of wide compositional PtRu alloys prepared by thermal decomposition. However, it was concluded that a ∼50:50 composition provided the best results at potentials above 0.3 V vs. RHE.

According to these previous results, it is reasonable to prepare the combinatorial array which has the various Pt compositions of 90–50% and find the active region by combinatorial screening after 20 times of cyclic voltammetry. And because the resolution of the large array is not sufficient to point to the most active composition, it is necessary of serial electrochemical analysis to find the optimal composition within the active region.

One of the important steps to prepare the combinatorial array is the selection of the third and forth metals. Many characteristics of the metals should be thoroughly considered to find the best Pt–Ru–M_1–M_2 compositions for methanol electro-oxidation and the results have to be supported with data available in the literature. It is well known that the binary mixture of Ru [12–16], Mo [23,24], and W [25] with Pt shows the electrocatalytic activity of methanol or H_2/CO mixture oxidation higher than Pt and it is supposed that tungsten and molybdenum are active as redox catalyst [19,20].

Considering that it has been suggested the strongly adsorbed CO as a reaction intermediate blocks the large portion of the polycrystalline Pt surface and that forms passive CO islands [26], we believe the third and fourth metals can easily provide the oxygenated species for CO_{ads} oxidation at low potential, mainly through water activation [27]. In detail, water binding energy to the metals has to be as high as possible and the activation energy of OH bond scission has to be as low as possible. Anderson et al. [28] reported the theoretical values of the above binding and activation energies of the various metals. According to them, Mo and W show the binding energy of 2.4 eV (2.6 eV for Ru) and the activation energy of 0.25 and 0.41 eV (0.31 eV for Ru).

Fig. 2 shows the fluorescence images at low and high overpotential and the high active regions in Pt–Ru–Mo–W quaternary compositions of which Pt compositions are 80 and 70% individually. In two cases, active regions are Ru-rich ones and small amount of Ru is replaced with Mo and W.

A chronoamperometry experiment in conjunction with stationary anode polarization with the catalyst-modified thin film glassy carbon electrode was used to compare the electrocatalytic activity of the prepared bulk catalysts with that of commercially available Johnson–Matthey Pt(50)Ru(50). The results of EDX, ICP and BET surface area measurements are summarized in Table 1. And the average particle size was also estimated from Pt(220) diffraction peaks according to the Scherrer formula [29]. In order to avoid the film-diffusion effects for the exact electrochemical characterization, the thickness of electrode is thin to have a metal loading on the glassy carbon electrode (6 mm diameter) of 284 $\mu g/cm^2$. Details of the preparation of the

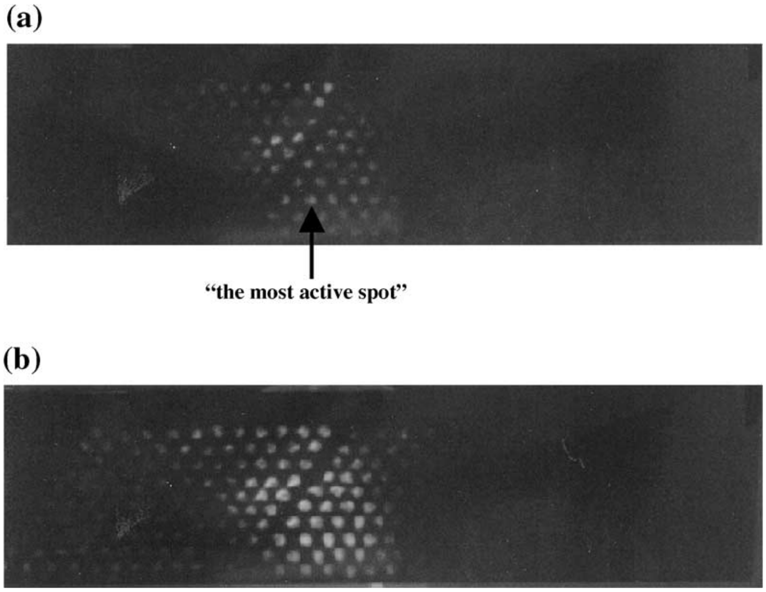

Fig. 2. Combinatorial array and screening results by fluorescence imaging. Active compositions for methanol electro-oxidation are shown as bright spots: fluorescence image (a) at lower overpotential (≈0.4 V vs. RHE) and (b) at higher overpotential (≈0.46 vs. RHE) after 20th cyclic voltammetry.

thin film electrodes have been reported elsewhere [30,31].

The activities for methanol electro-oxidation can be quantified as a steady-state current density at a constant potential. Fig. 3 shows the current measured for 1 h as the potential was stepped from 0.075 to 0.45 V vs. RHE for the electrode immersed in a solution of 2 M CH_3OH in 0.5 M H_2SO_4 at 25 °C. And after the potentiostatic oxidation, the same catalyst-modified thin film glassy carbon electrodes, which were used in the above experiments, were also characterized by stationary anode polarization curves, and their results are shown in Fig. 4.

Table 1
Properties of catalyst materials[a]

Catalyst	Surface area (m^2/g)	Particle size (nm)
Pt(50)Ru(50)	78.76	2.46
Pt(82)Ru(18)[b]	65.81	3.89
Pt(74)Ru(20)Mo(4)W(2)[c]	50.52	3.23
Pt(77)Ru(17)Mo(4)W(2)[c]	83.10	3.43

[a] Numbers in parentheses are bulk compositions (at.%).

[b] Bulk compositions obtained from EDX results.

[c] Bulk compositions obtained from ICP results.

From these results (Figs. 3 and 4), it can be known that there is a clear range of catalytic activities even with the small composition difference of the catalysts. And the quaternary catalyst, Pt(77)Ru(17)Mo(4)W(2), identified from combinatorial screening results is superior to the other catalysts including commercially available Johnson–Matthey Pt(50)Ru(50) and able to provide the higher current density, supposedly because of the advanced CO_{ads} oxidation activity.

As far as we know, quaternary PtRuMoW catalyst for methanol electro-oxidation has not been reported. And it is difficult to identify the exact role of Mo and W during methanol electro-oxidation in such catalyst. Lasch et al. [31] reported that introduction of a transition metal oxide like WO_x, MoO_x and VO_x to PtRu binary catalysts led to an improvement of catalytic activity towards methanol oxidation and it was resulted from the redox process of the transition metal oxides. Götz and Wendt [20] also found a promoting effect of tungsten when combined to PtRu catalyst and reported a further increase in activity could be achieved by optimization of the molar ratios of the metals in the ternary PtRuW catalyst system. More recently, encouraging results with Pt(70)Ru(26)Mo(4) ternary

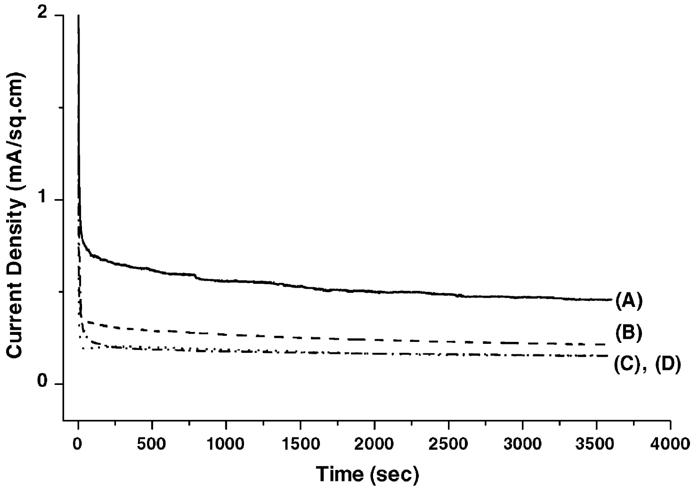

Fig. 3. Methanol electro-oxidation activities of catalyst materials: (A) Pt(77)Ru(17)Mo(4)W(2); (B) Pt(74)Ru(20)Mo(4)W(2); (C) Pt(50)Ru(50); and (D) Pt(82)Ru(18). Potentiostatic oxidation of 2 M CH_3OH in 0.5 M H_2SO_4 deaerated with ultrahigh purity N_2 at 25 °C during the potential-step from 0.075 to 0.45 V vs. RHE.

catalysts were observed at low potential for methanol electro-oxidation by Lima et al. [27].

In the case of the addition of non-noble metals to platinum, it should be considered deeply whether they can be stable or not in acidic condition. And the corrosion of the additive metals can be misunderstood as a real catalytic activity [32]. Whether the stable compositions can be made depend on phase equilibria (e.g., because the solubility limit of Mo in the Pt f.c.c. lattice is 20%, single phase Pt(50)Mo(50) cannot be made) [10]. Since Mo and W are present at an atomic ratio of 6% totally and quaternary PtRuMoW catalysts are far more complex, we can make assumption that Mo and W in this system are stabilized by being present in the PtRu structure so that they can provide oxygenated species at low potential.

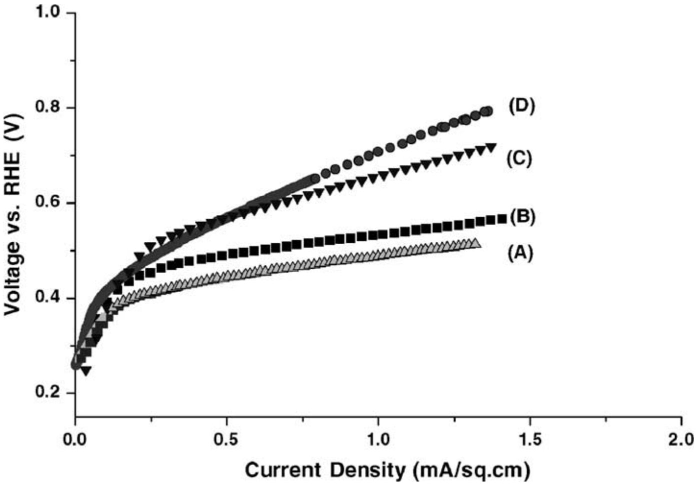

Fig. 4. Methanol electro-oxidation activities of catalyst materials; anode polarization curves of 2 M in 0.5 M H_2SO_4 deaerated with ultrahigh purity N_2 at 25 °C. The compositions correspond to those in Fig. 3.

4. Conclusions

In conclusion, the repeated cyclic voltammetry makes the combinatorial method using fluorescence indicators expand into a screening tool to find the catalyst that not only showing an initial excellent performance but also being active in the long-run reaction. Future studies from our laboratory will address the physicochemical properties of this newly found Pt-based catalyst to find out the plausible explanation why the small addition of Mo and W to PtRu increased the catalytic activity in methanol electro-oxidation.

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