

Dispersed platinum and tin polyaniline film electrodes for the anodes of the direct methanol fuel cell

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Abstract To develop better and cheaper electrocatalysts for the oxidation of methanol in direct methanol fuel cells, several combinations of a conductive polymer polyaniline (PANI) and dispersed metal particles such as Pt and Sn were examined. The anodic current for the methanol oxidation (i_{MeOH}) showing the electrocatalytic activity of Pt particles was remarkably enhanced when the particles were dispersed on PANI films that should provide higher surface areas for the dispersed particles. The activity strongly depended on the morphology and the electric conductivity of the PANI films electropolymerized in five different acid solutions: H_2SO_4 , HNO_3 , HClO_4 , HBF_4 , and HCl . The highest activity was achieved using the dispersed Pt particle on PANI film electropolymerized from H_2SO_4 polymerizing solution. In order to reduce the dispersed amount of the expensive Pt particles, other metal particles were pre-dispersed on the PANI film prepared from the H_2SO_4 polymerizing solution, and then Pt particles were dispersed on the film. Among the pre-dispersed metal particles attempted here (Sn, Cu, Cr, Ni, In, Co, Sb, Bi, Pb, and Mn), the highest activity was obtained with Sn particles. When the ratio of dispersed Pt to Sn particles ranges from 32:68 to 100:0, i_{MeOH} is higher than that measured with the dispersed Pt particle on PANI films

without the Sn particles. This means that the dispersed amount of the Pt particles could be reduced by utilizing dispersed Sn particles.

Keywords Methanol oxidation · Direct methanol fuel cell · Tin · Platinum · Electrocatalyst

Introduction

Much attention has been given to fuel cells in recent years because they can directly convert chemical energy to electrical energy with higher efficiency than other sources of electrical power. Among fuel cells, the direct methanol fuel cell (DMFC) is one of the most attractive ones because it requires no methanol reforming processes needing high-pressure vessels and because methanol is effectively converted into electrical energy from its liquid state, which is advantageous in methanol transfer [1–4]. Unfortunately, however, the DMFC has at least two problems to be solved for practical use: (1) it requires expensive electrocatalysts such as Pt for the methanol oxidation and the electrocatalytic efficiency is relatively low; (2) the active sites of the electrocatalysts are poisoned by the adsorption of reaction intermediates such as CO [5–8].

A promising strategy for alleviating these problems is the introduction of conductive polymers. Polymers have been widely employed as porous supports on which to disperse the electrocatalysts. The dispersion can decrease the poisoning effect described previously as a problem (2) [9, 10]. Among the polymers, polyaniline (PANI) is one of the best candidates because it can easily be prepared on the electrode substrate as a homogeneous and strong adherent film with a high surface area and good stability in acid media [11–14]. Although some promising results have been

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reported and the highest electrocatalytic activity is obtained for dispersed Pt particles on PANI film [15–24], the electrocatalytic activity has to be enhanced further for practical use. In addition, every needed effort should be made to decrease the amount of the expensive Pt particles.

In this communication, in order to decrease the amount of the Pt particles, Pt and other metal particles (Cr, Ni, In, Co, Sb, Bi, Pb, and Mn) were simultaneously dispersed on the PANI films by cathodic electrodeposition. The electrocatalytic activity was examined using the dispersed metal and Pt particles on PANI films. The highest activity is obtained for the dispersed Sn and Pt particle on PANI films, and the activity is almost the same as that of the dispersed Pt particle on PANI films without the Sn particles.

Experimental details

A standard three-electrode cell was employed, comprising of glassy carbon (GC) disc electrodes with an electrode area of 0.196 cm^2 , a commercial Ag/AgCl electrode, and a Pt plate counter electrode. The GC disk electrodes were polished with alumina powder prior to use. Electrochemical experiments were carried out with a Hokuto Denko HZ-3000 potentiostat connected to a Rikadenki RY-101 x - y recorder.

The monomer, aniline (Katayama Chemicals Co.), was of reagent grade and was distilled under reduced pressure prior to use. Other chemicals were of analytical grade and were used as received. Aqueous solutions were prepared using distilled and deionized water. The PANI films were electrochemically deposited by constant-potential electropolymerization at $+0.8 \text{ V}$ onto the GC electrodes in aqueous acidic solution containing 0.20 M ($1 \text{ M}=1 \text{ mol dm}^{-3}$) aniline ($[\text{H}^+]=1.0 \text{ M}$) under N_2 atmosphere at $25 \text{ }^\circ\text{C}$. The deposited amount of the PANI films was controlled by the charge passed during the electropolymerization, and the amount was approximately $170 \text{ } \mu\text{g cm}^{-2}$. The PANI film-covered electrodes were reduced electrochemically in $0.5\text{-M H}_2\text{SO}_4$ aqueous acidic solution ($[\text{H}^+]=1.0 \text{ M}$) at -0.2 V until the current reached background level.

Platinum particles were dispersed on the PANI films by electrodeposition from 1.0-M HCl solution containing $0.02 \text{ wt.}\%$ $\text{H}_2[\text{PtCl}_6]$ at a constant current of $50 \text{ } \mu\text{A cm}^{-2}$. Likewise, the other metal particles were dispersed from protonic acid solutions containing $0.02 \text{ wt.}\%$ of the corresponding metal ions at a constant current of $50 \text{ } \mu\text{A cm}^{-2}$. The deposited amount of the metal particles was determined by the charge passed during the electrodeposition.

The morphology of the obtained PANI film was observed using a Hitachi S-2300 scanning electron microscope (SEM).

Results and discussion

Figure 1 shows the cyclic voltammogram of the dispersed Pt particle PANI film measured in aqueous 0.5-M ($1 \text{ M}=1 \text{ mol dm}^{-3}$) H_2SO_4 solution and in H_2SO_4 solution containing CH_3OH . The redox current of PANI appears around 0.3 and 0.6 V . The anodic peak current at 0.82 V is ascribable to the oxidation of CH_3OH . The electrocatalytic activity was evaluated by the anodic current (i_{MeOH}), which was calculated by subtracting the background current in the absence of CH_3OH .

We have shown that i_{MeOH} for the dispersed Pt particle on PANI film electrode was about three times as large as the i_{MeOH} for the dispersed Pt particle electrode without the PANI film [25]. There is no doubt that i_{MeOH} is influenced by the conductivity and morphology of the PANI film. Both the conductivity and morphology could be changed by the type of dopant anion, in other words, the type of acid for the polymerizing solution [14, 26–29]. To determine the best acid for the largest i_{MeOH} value, by electropolymerizing aniline in five polymerizing solutions containing different acids, we prepared five electrodes covered with PANI films having different dopant anions: SO_4^{2-} , NO_3^- , Cl^- , BF_4^- , and ClO_4^- . The Pt particles were then dispersed on the PANI films. Figure 2 shows how i_{MeOH} depends on the dopant anions. For comparison, i_{MeOH} for the PANI films without Pt particles is also shown. In any case, i_{MeOH} is enhanced by the presence of the PANI film. This enhancement is probably due to a substantial decrease in the poisoning species for Pt such as CO, which are intermediate products [9]. The largest i_{MeOH} is observed for the SO_4^{2-} -doped PANI film. In addition, little difference in i_{MeOH} is seen between the five PANI films without dispersed Pt particles.

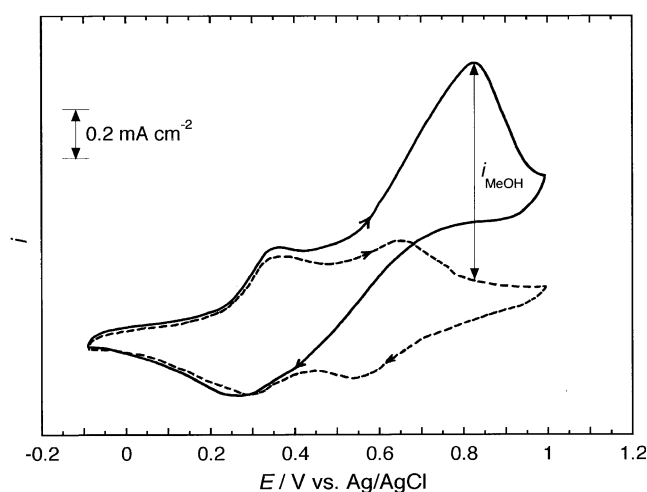


Fig. 1 Cyclic voltammograms at 20 mV s^{-1} of the dispersed Pt particle on PANI films measured in $0.5\text{-M H}_2\text{SO}_4$ solution containing $10\text{-M CH}_3\text{OH}$ (—) and in $0.5\text{-M H}_2\text{SO}_4$ solution (---). The deposited amount of the PANI film, $170 \text{ } \mu\text{g cm}^{-2}$; the dispersed amount of the Pt particles; $101 \text{ } \mu\text{g cm}^{-2}$

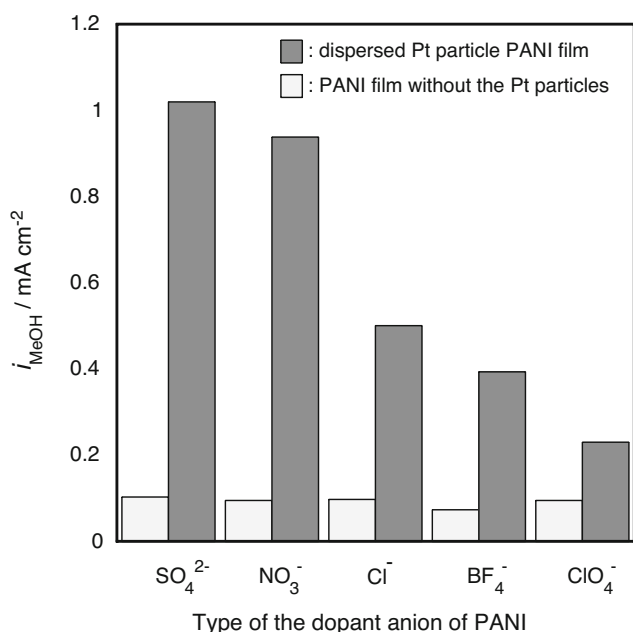


Fig. 2 Effect of the type of the PANI dopant anion on i_{MeOH} . The deposited amount of the PANI film, $170 \mu\text{g cm}^{-2}$; the dispersed amount of the Pt particles: $101 \mu\text{g cm}^{-2}$

Although we have no evidence to clarify why the SO_4^{2-} -doped PANI film is the most effective, we speculate that the highest electrocatalytic activity is strongly related to morphology and conductivity. The morphology and conductivity depends on the type of the dopant anion and the dependence varies in the electropolymerization conditions. For example, some reports say that the ClO_4^- - or BF_4^- -doped PANI film has a fibril structure, while the SO_4^{2-} - or NO_3^- -doped one is granular [26–29]. Others say that the granular structure is seen for the BF_4^- -doped one, while the fibril structure is for the SO_4^{2-} - or NO_3^- -doped one [14, 30]. To examine the morphology dependence in our electropolymerization conditions, the surface of the PANI films were observed by the SEM. The SEM observation revealed that the surface of the Cl^- , NO_3^- , ClO_4^- , or BF_4^- -doped PANI film has the fibril structure, while that of the SO_4^{2-} -doped one was not granular but a unique leafage structure. The Pt particles are effectively dispersed on the PANI film with this leafage structure. In addition, we are examining why the effective dispersion is achieved on the PANI film with the leafage structure and the reason will be published elsewhere (Yano et al., manuscript in preparation).

In order to relatively reduce the dispersed amount of expensive Pt particles, we dispersed other metal particles on the SO_4^{2-} -doped PANI film prior to the dispersion of the Pt particles. Ten metals (Mn, Pb, Bi, Sb, Co, In, Ni, Cr, Cu, and Sn) were employed and dispersed by constant-current electrodeposition at $50 \mu\text{A cm}^{-2}$ up to a passed charge of 50mC cm^{-2} . Figure 3 illustrates which metal is effective as dispersed particles. As can readily be seen in any case, the

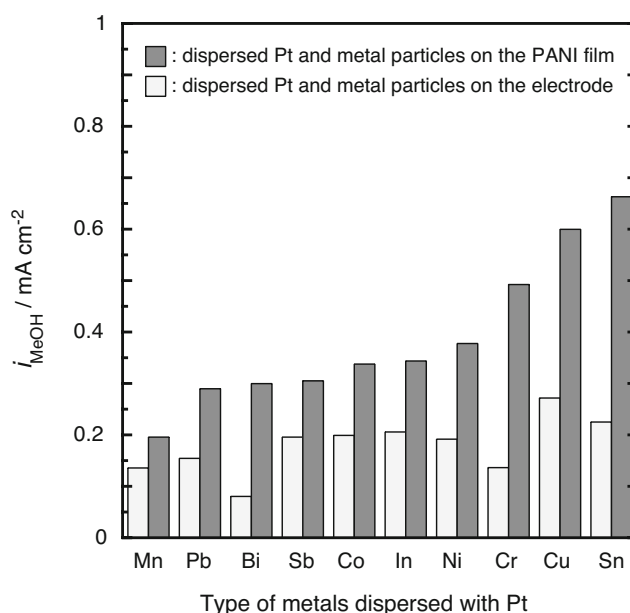


Fig. 3 Effect of the type of metal particles dispersed with Pt particles on i_{MeOH} . The deposited amount of the PANI film, $170 \mu\text{g cm}^{-2}$

PANI film significantly enhances the i_{MeOH} value and the enhancement differs with the kind of the metals. The largest i_{MeOH} value was obtained for Sn, although we have not clarified the reason.

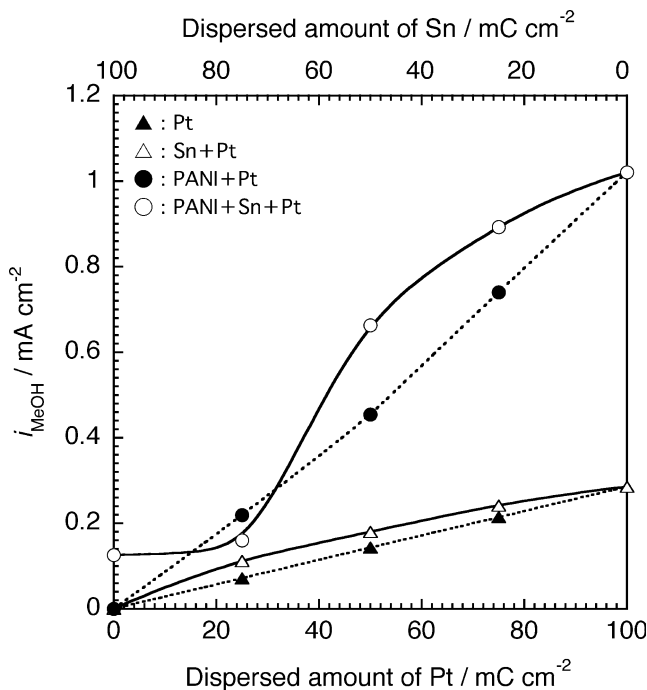


Fig. 4 Relationship between the relative ratio of the dispersed Sn to Pt particles and i_{MeOH} . Filled triangle, dispersed Pt particles on the carbon electrode. Open triangle, dispersed Pt and Sn particles on the carbon electrode. Filled circle, dispersed Pt particles on the PANI film. Open circle, dispersed Pt and Sn particles on the PANI film. The deposited amount of the PANI film: $170 \mu\text{g cm}^{-2}$

Because Sn turned out to show the highest electrocatalytic activity as the particles dispersed with the Pt particles, we next examined the effect of the relative ratio of the dispersed Sn to Pt on i_{MeOH} . The ratio was intentionally changed by the charge passed during the electrodeposition of Sn and Pt, and, in any case, the charge was 100 mC cm^{-2} , which corresponded to $61.5 \text{ } \mu\text{g cm}^{-2}$ for Sn and $101 \text{ } \mu\text{g cm}^{-2}$ for Pt. The relationship between the ratio and i_{MeOH} is shown in Fig. 4. As can readily be seen in Fig. 4, the positive effect of the dispersed Sn is evident except for the case where the dispersed amount of Pt is 25 mC cm^{-2} and that of Sn is 75 mC cm^{-2} . In any case, without the PANI film (see the two curves at the bottom), i_{MeOH} is enhanced when the Sn particles are dispersed with the Pt particles. The magnitude of the enhancement is further increased by the presence of the PANI film. Furthermore, it is interesting to find that i_{MeOH} is observable for the dispersed Sn particle on PANI film without the dispersed Pt particles, while no i_{MeOH} is seen for the other cases without the dispersed Pt particles. These results are practically useful because Sn could replace the expensive Pt.

There is no doubt that the PANI film plays a significant role in the electrocatalytic reaction. This role is probably based on the following two facts: adsorption of the intermediate species and high dispersion of the Pt particles, in other words, a large surface area for the Pt particles. According to a study using electrochemically modulated infrared reflectance spectroscopy [9], the PANI film adsorbs the intermediate species such as CO, which act as poisoning species for Pt. The adsorption prevents the dispersed Pt particles from becoming deactivated. On the other hand, in order to confirm whether the PANI film promotes effective Pt dispersion, the size of the Pt particles was calculated based on the charge required for the hydrogen adsorption and desorption. The average diameter of the dispersed Pt particles directly on the carbon electrode was $0.12 \text{ } \mu\text{m}$, while that on the PANI film was $0.23 \text{ } \mu\text{m}$.

Little is known about why the dispersed Sn particles are effective. It was recently reported that adsorbed CO coming from the ethanol dissociative chemisorption is greatly reduced by modifying the composition of the Pt anode by adding Sn during the electrooxidation of ethanol [30]. Likewise, the Sn particles may reduce the adsorbed CO during the electrooxidation of methanol. Anyway, the

dispersed Sn and Pt particles on PANI film are expected to be useful for the anode of the DMFC because these reduce the cost.

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