Effect of reduction temperature and second metal addition to Pd catalysts for formic acid oxidation

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Abstract: Palladium is known to be effective for formic acid oxidation. The effect of Pd particle size and second metal addition to Pd were investigated to improve activity and stability in formic acid oxidation in a neutral condition. Pd/C catalyst reduced at 450°C was the best compromise of mass activity (surface area) and stability. Nickel addition to Pd gave higher mass activity, but an excess Ni was found to form large particles during potential cycles. High surface area obtained by dissolution of second metal has significant influence on the performance in the case of Pd-Ni catalyst.

Keywords: palladium, bimetallic catalyst, formic acid oxidation.

1. Introduction

Formic acid is one of the alternative fuels for low temperature fuel cells. Palladium is known to be effective for formic acid oxidation compared to platinum, since formic acid is oxidized directly to CO_2 on Pd[1] while an indirect pathway via poisonous CO and formate intermediates is accompanied on Pt catalyst[2]. The intermediate in the direct pathway to CO_2 is under debate, but weakly adsorbed $HCOO^-$ has been considered historically as active intermediates[3]. The structure and composition of catalyst impact the reaction pathway. Close interparticle distance has been reported to cause the indirect pathway with poisonous species[4]. Copper addition to Pd was reported to promote formic acid oxidation through modification of electronic and surface structures[5]. However, importance of each factor to the catalytic functions is yet to be clarified.

In the present study, the effects of Pd loading and heat treatment temperature were investigated in order to clarify the size effect on both activity and stability. The effect of second metal (Ni, Cu, Au) addition was also compared to examine the contributions of surface and electronic structures of Pd to the catalytic performance.

2. Experimental

Palladium-based catalysts were prepared by impregnation methods. Carbon black (Ketjen EC600JD) was impregnated with palladium(II) acetate and nickel nitrate at 1:0.3 (co-impregnation) and 1:7 (sequential impregnation aiming at Pd segregation on the surface) of Pd:Ni atomic ratios keeping Pd loading at 5.4 wt.%. After impregnation, the sample was reduced in a hydrogen stream. The catalysts were characterized by X-ray diffraction (XRD: MultiFlex, Rigaku), transmission electron microscope (TEM: JEM-2100, JEOL), and CO stripping voltammetry. Catalytic activity for formic acid oxidation was measured by cyclic voltammetry (CV) using a three-electrode cell. After potential cycling in an electrolyte solution (0.1 M Na_2SO_4) for surface cleaning, the oxidation current was measured by CV in the solution containing 0.185 M sodium formate in a potential range from −0.80 to 1.00 V vs. Ag/AgCl electrode at a scan rate of 0.1 V/s at 30°C. Prior to testing various catalysts, the solution pH and formic acid concentration were optimized using monometallic Pd catalyst.

3. Results and discussion

Cyclic voltammetry (CV) was carried out in an aqueous electrolyte at pH=7 where the highest current was obtained. Among Pd catalysts reduced at different temperatures, Pd reduced at higher temperature showed higher stability (Fig. 1(a)). The electrochemical active area (ECA) was in the order of the samples reduced at 550ºC < 300ºC < 450ºC, which is in agreement with formic acid oxidation activity in the early cycles. A weak XRD peak of Pd(111) for the sample reduced at 300ºC indicates that a part of Pd exists in a form of fine or low-crystalline particles, which would cause rapid particle growth during the potential cycles. Meanwhile, the electrochemical surface area (ECSA) of the sample reduced at 550ºC was much smaller than those of other samples, suggesting that sintering occurs above 450ºC. The Pd sample reduced at 450ºC showed a best compromise between activity and stability.

Pd-Ni catalyst with high Ni content showed higher activity than monometallic Pd/C at the early cycles, but the activity rapidly decreased within 5 cycles (Fig. 1(b)). The TEM images of fresh and used catalysts showed that nickel particles became a few times larger in size after 50 cycles (Fig. 2). It is possible that severe Ni dissolution causes a large amount of exposed Pd on the surface, but such Pd could grow easily. On the other hand, Pd-Ni catalyst with low Ni content maintained higher current than Pd/C. Since the peak current increased when the upper limit of the potential range was extended in CV, it is suggested that Ni in this catalyst moderately dissolves during the potential cycles increasing the surface area of Pd. The Pd-Cu and Pd-Au catalysts showed smaller or negligible enhancement of monometallic Pd. Thus, change in surface structure through dealloy has a significant impact as well as electronic modification by second metal.

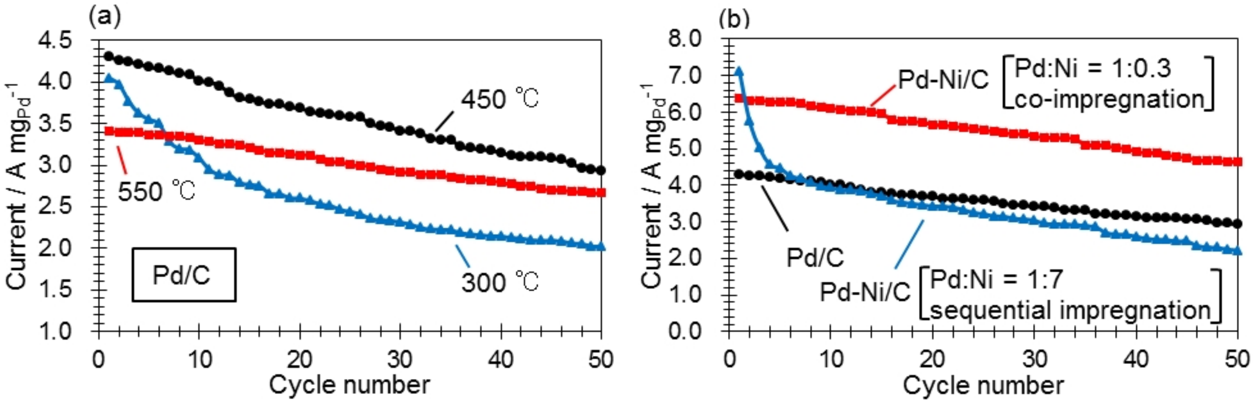

Figure 1. Change in peak current during cyclic voltammetry. (a) Comparison of Pd/C catalysts reduced at different temperatures; (b) comparison of Pd/C and Pd-Ni catalysts. Conditions: 0.185 M HCOONa + 0.1 M Na_2SO_4 at 30ºC; scan range: −0.8 ~1.0 V; scan rate: 0.1 V/sec.

4. Conclusions

Cyclic voltammetry was carried out for Pd catalysts reduced at different temperatures and Pd-M bimetallic catalysts in a formate-containing neutral electrolyte where the highest current is obtained. Pd-Ni catalyst with low Ni content kept higher current than Pd catalyst during the CV while Pd-Ni catalyst with high Ni content gave higher current only in initial cycles. The activity enhancement was larger for Pd-Ni than the case of Pd-Cu, which suggests that modification of surface structure has a larger impact than electronic modification in the present reaction condition.

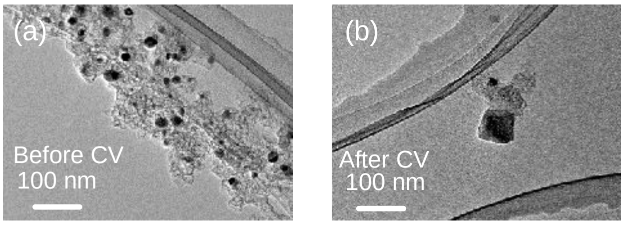

Figure 2. TEM images of Pd-Ni catalyst with high Ni content. (a) Before CV; (b) after CV.

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