

Short Communication

Glycerol Oxidation on Pd Electrodes Modified with Pt

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The electrocatalytic oxidation of glycerol on Pd electrode modified with Pt is investigated. The Pt-modified Pd electrodes with different Pt loadings are prepared by means of potentiostatic deposition of Pt on polycrystalline Pd electrodes. Scanning electron microscope (SEM) images show that the Pd substrate is partially covered by the Pt nanoparticles of different sizes. The Pt modification leads to an improvement in the catalytic activity of the Pd electrode for glycerol oxidation in alkaline solution, and the activity of the Pt-modified Pd electrodes has a close relation to the amount of the deposited Pt. In a wide range of the Pt loadings, the Pt-modified Pd electrodes show higher catalytic activity than Pd and Pt electrodes in terms of oxidation potential and peak current density.

Keywords: Glycerol; Oxidation; Electrode; Modification; Catalytic activity

1. INTRODUCTION

Glycerol is a renewable chemical, and its supply increases since glycerol is largely produced as a byproduct in the transesterification of fatty acids into biodiesel. Many useful chemicals can be produced from glycerol by different reactions, and considerable efforts have been made to find new applications of glycerol [1,2]. In recent years, the electrocatalytic oxidation of glycerol has been attracted an increasing interest for its potential use in fuel cells and electrochemical synthesis [3–7]. For example, in cogeneration of both electricity and valuable chemicals by the electrocatalytic oxidation of glycerol on Pt/C catalyst in anion-exchange membrane fuel cell, the highest selectivity of glyceric acid and tartronic acid can reach 91% [4]. Besides of Pt, Pd and Au [8–14], bimetallic and trimetallic nanoparticulate catalysts based on these metals, such as PtRu/C [15], PtRu/grapheme [16], PtBi/C and PdBi/C [17], PtAu/C [18], PdAu/C [9,19], PtNi/C [20], PtRuSn/C [21], and PtPd/Ru [22], are widely used in the electrocatalytic oxidation of glycerol.

Surface modification is one of the efficient methods to improve the activity and stability of metal electrode and is also useful for the preparation of electrocatalysts by using as less noble metal as possible. The surface modification of substrate metals like single crystal and polycrystalline Au, Pt and Ag with various second metal adatoms has been intensively investigated [23–25], and great progresses have been made in the modification method and structure analysis. The surface modification of Pd substrates with other metal and its application in electrocatalytic reactions have also been reported, such as the preparation of Pt monolayer on Pd(111) surface and on carbon-supported Pd nanoparticles through the galvanic displacement by Pt of an underpotentially deposited Cu monolayer on the Pd substrates and its application in O₂ reduction [26], the synthesis of Pt-on-Pd/C catalysts by the sequential thermal decomposition of Pd acetylacetonate and Pt acetylacetonate and its application in O₂ reduction [27], the preparation of Au-covered Pd nanowire arrays by the Au replacement of Pd in a HAuCl₄ solution and its application in ethanol oxidation [28], and the Bi modification of Pd through the immersion of Pd/GC electrode in an acidic solution containing Bi(NO₃)₃ and its application in the oxidation of aliphatic aldehyde [29], but the papers on this subject are very limited. On the other hand, Pt and Pd are widely used to modify other substrate metal.

Glycerol oxidation on Pt and Pd electrodes in alkaline solution shows more negative oxidation potential (onset potential and peak potential) but significantly low peak current density as compared to that on Au electrode [10,12]. Few papers about glycerol oxidation on the metal electrode modified with second metal adatoms have been published. In this study, the surface modification of Pd substrate with Pt adatoms has been investigated to increase the catalytic activity of the electrodes for glycerol oxidation, and the result shows that the electrochemical modification of Pd with Pt is a simple and effective method for this purpose. Pt-modified Pd electrodes show interesting behaviors in glycerol oxidation.

2. EXPERIMENTAL

Polycrystalline Pd and Pt electrodes with a diameter of 4 mm embedded in PTFE were used in the experiments. The Pd and Pt electrodes were polished with alumina (down to 0.03 μm) slurry and cleaned ultrasonically in water prior to use. A Pt coil was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode in both the surface modification and glycerol oxidation. The surface modification of Pd electrode with Pt was carried out by depositing Pt at +0.20 V vs. SCE in a solution of 0.05 mol L⁻¹ H₂SO₄ + 1.0 mmol L⁻¹ H₂PtCl₆. The amount of Pt was controlled by the deposition time, and Pt-modified Pd electrodes with different Pt loadings were prepared.

The Pt-modified Pd electrode was then rinsed with water and transferred to an electrochemical cell containing a 0.5 mol L⁻¹ NaOH + 0.1 mol L⁻¹ glycerol solution, and cyclic voltammetric (CV) measurement was conducted. All measurements were performed at a room temperature of about 25 °C. In this paper, the Pt-modified Pd electrodes are denoted as Pt_(t)/Pd in which *t* represents the time of the *t* deposition, and potentials are reported with respect to SCE.

3. RESULTS AND DISCUSSION

3.1. Surface modification of Pd electrode with Pt

In this study, the potential of +0.20 V selected for the deposition of Pt is more negative than the Nernst potential, so the deposition is an overpotential deposition. The Pt deposition was performed for 5, 10, 20, 30, and 40 s, respectively, and the charge of 58, 112, 225, 296, and 383 μC was obtained correspondingly by the Pd electrode (4 mm in diameter). From the above charge values, the Pt loadings of 0.23, 0.45, 0.91, 1.20 and 155 $\mu\text{g cm}^{-2}$ in terms of the geometric surface area of the Pd substrate were obtained for Pt_(5s)/Pd, Pt_(10s)/Pd, Pt_(20s)/Pd, Pt_(30s)/Pd and Pt_(40s)/Pd electrodes. It can be seen that the range of the Pt loadings examined is relatively wide, but on the whole the Pt loadings are low.

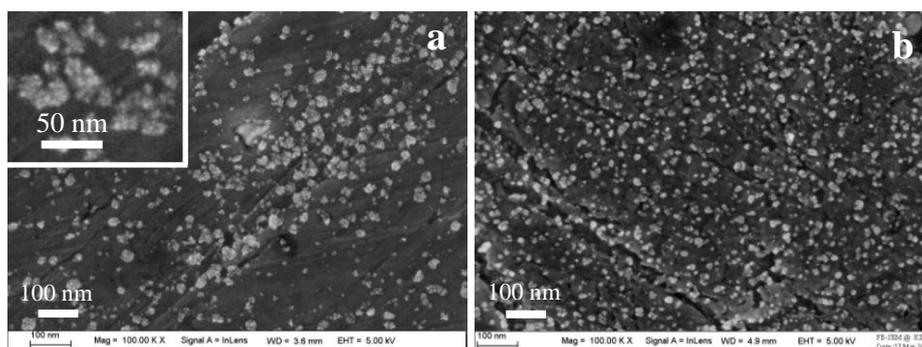


Figure 1. SEM images of (a) Pt_(10s)/Pd and (b) Pt_(20s)/Pd electrodes.

The SEM images of Pt_(10s)/Pd and Pt_(20s)/Pd electrodes in Fig. 1 display that the Pt nanoparticles of different sizes are distributed on the Pd substrates and the large part of the Pd substrates is not covered by the deposited Pt. The Pt nanoparticles are found to be not evenly distributed on the Pd substrate. This is believed to be largely related to the uneven Pd surfaces, since the Pd substrates were polished with alumina slurry prior to the deposition of Pt. The inset in Fig. 1a further reveals that the larger Pt nanoparticles are formed by the aggregation of many smaller ones. Fig. 1(a and b) further shows that, with increasing Pt loading, more Pt particles are formed and the distribution of the Pt particles gets denser, but the particle size has no significant variation.

Figure 2 shows the CVs of Pt, Pd and some typical Pt/Pd electrodes in a H₂SO₄ solution. The broad and low cathodic peak at ca. +0.45 V on the Pt electrode represents the reduction of Pt oxide, and the sharp and high cathodic peak at ca. +0.43 V on the Pd electrode represents the reduction of Pd oxide. It is interesting to notice that though onset potential and peak potential of the oxide reduction peaks on the Pt/Pd electrodes are slightly more negative than those on the Pd electrode, the shape of the peaks is similar to that on the Pd electrode rather than that on the Pt electrode, regardless of the amount of the deposited Pt. Furthermore, it is seen that the oxide reduction peak on the Pt/Pd electrodes gradually decreases with increasing Pt loading. Similar behaviors were reported for PtPd/C catalyst, in which PtPd/C of higher Pd content shows a higher oxide reduction peak [30]. Due to the

overlap of the Pd oxide reduction peak and Pt oxide reduction peak, it is difficult to evaluate the electrochemically active surface area of Pt and Pd for the Pt/Pd electrodes.

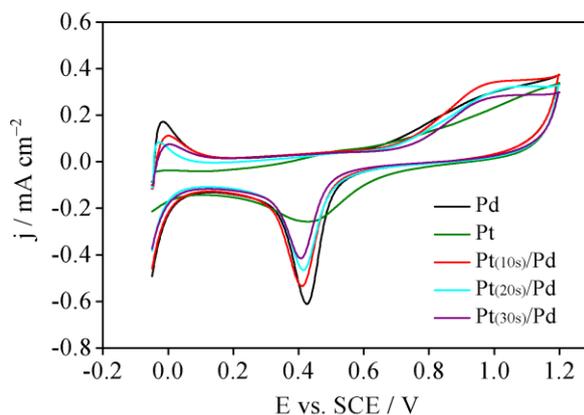


Figure 2. CVs of Pd, Pt and some typical Pt/Pd electrodes in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. Scan rate: 50 mV s^{-1} .

3.2. Glycerol oxidation on Pt-modified Pd electrodes

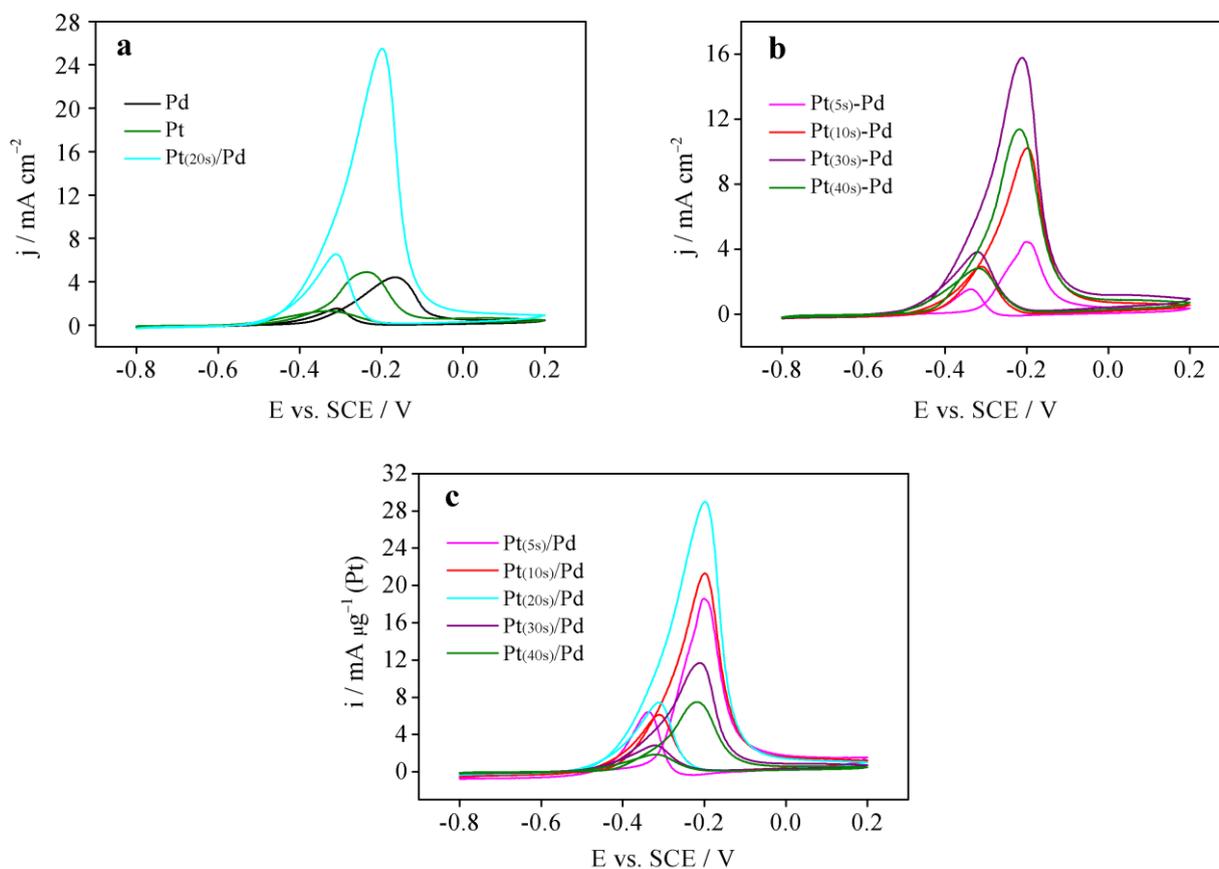


Figure 3. CVs of Pd, Pt and Pt/Pd electrodes in $0.5 \text{ mol L}^{-1} \text{ NaOH} + 0.1 \text{ mol L}^{-1} \text{ glycerol}$. Current density is normalized to per unit geometric surface area of the Pd substrate (a and b) and per unit mass of the Pt loading (c). Scan rate: 50 mV s^{-1} .

Fig. 3a shows the CVs of Pt, Pd and Pt_(20s)/Pd electrodes, in which the current density is normalized to per unit geometric surface area of the corresponding substrate. The peak at -0.24 V with the peak current density of 4.9 mA cm^{-2} on the Pt electrode and the peak at -0.17 V with the peak current density of 4.4 mA cm^{-2} on the Pd electrode are observed. The peak on the Pt electrode shows more negative onset oxidation potential and peak potential and a little higher peak current density than that on the Pd electrode. Zhang et al. [12] reported a similar result. At the same time, glycerol oxidation on the Pt_(20s)/Pd electrode shows a peak at -0.20 V with the peak current density of 25.5 mA cm^{-2} . The peak current density on the Pt_(20s)/Pd electrode is more than five times higher than that on Pt and Pd electrodes, which indicates high catalytic activity of the Pt_(20s)/Pd electrode.

The Pt/Pd electrodes with different Pt loadings were used in the experiments to investigate the effect of the amount of the deposited Pt on the activity of the Pt/Pd electrodes towards glycerol oxidation, and the results are shown in Fig. 3b. The peaks display a gradual negative shift of onset oxidation potential and peak potential and an increase and then a decrease of peak current density with increasing Pt loading. The sequence of the peak current densities is Pt_(20s)/Pd > Pt_(30s)/Pd > Pt_(40s)/Pd > Pt_(10s)/Pd > Pt_(5s)/Pd, with the peak current density on the Pt_(5s)/Pd electrode being nearly the same as that on the Pd electrode and the peak current density on the Pt_(10s)/Pd electrode being higher than that on the Pt electrode. The result suggests the impact of the Pt loading on the catalytic activity of the Pt/Pd electrodes: when an appropriate amount of Pt is deposited on the Pd substrate, the Pt/Pd electrode shows higher catalytic activity than Pt and Pd electrodes, and a Pt/Pd electrode with the right amount of the Pt loading shows the highest activity; when the Pt loading is very low, the role of Pt in the function of the Pt/Pd electrode is limited, thus the property of the Pt/Pd electrode is mainly determined by the Pd substrate and the activity of the Pt/Pd electrode will be similar to that of the Pd electrode; when the Pt loading is high, the role of the Pd substrate is limited, so the activity of the Pt/Pd electrode will be similar to that of the Pt electrode.

Comparing the CVs of the Pt/Pd electrodes with that of the Pd electrode reveals the difference in the catalytic activity of the Pd electrode before and after the Pt modification, and the improvement in the catalytic activity of the Pd electrode by the Pt modification in terms of oxidation potential and peak current density can be clearly seen. (i) Both onset potential and peak potential of glycerol oxidation on the Pt/Pd electrodes are more negative than those on the Pd electrode. Even a small amount of the deposited Pt results in a negative shift of oxidation potential, though it has no obvious impact on peak current density, as seen from the CV of the Pt_(5s)/Pd electrode. Peak potential shifts more negatively and gets close to that on the Pt electrode with increasing Pt loading, since the role of the deposited Pt increases while the role of the Pd substrate decreases. (ii) More obvious improvement is reflected in the reaction current. In the range of the Pt loadings examined, the peak current density on the Pt/Pd electrodes is higher than or at least the same as that on the Pd electrode. More negative oxidation potential and higher peak current density on the Pt/Pd electrodes than those on the Pd electrode suggest that the Pt modification is effective for improving the catalytic activity of the Pd electrode towards glycerol oxidation. Similarly, comparing the CVs of the Pt/Pd electrodes with that of the Pt electrode reveals the advantage of the Pt/Pd electrodes over the Pt electrode in catalytic activity. The peak on the Pt/Pd electrodes, except for the Pt_(5s)/Pd electrode, shows nearly the same onset oxidation potential but higher peak current density than that on the Pt electrode.

The enhanced catalytic activity of the Pt/Pd electrodes is mainly attributed to the following factors. (i) The difference in the function mechanisms of the different electrodes. Pd is more oxophilic than Pt, and the binding energy of hydroxyl is weaker on Pt_{ML}/Pd(111) than on Pt(111) and Pd(111) [31,32]. Therefore, the difference in the adsorption and reaction of glycerol and OH⁻ on Pd, Pt and Pt/Pd electrodes can be expected, which leads to different reaction rates between glycerol and hydroxyl on these electrode surfaces. Arenz et al. [31] reported that because of the very strong Pd–OH_{ad} bond, the catalytic activity of OH_{ad} towards the oxidation of CO_{ad} is significantly reduced on 1 monolayer Pd-modified Pt(111) in comparison with OH_{ad} which is adsorbed on Pt(111). Zhang et al. [26] reported that in a pseudomorphic Pt monolayer on Pd substrates, the effect of the d-band filling of the substrate is expected to be slight since the fractional filling of the d-bands of Pd and Pt is the same, and due to a mismatch between the lattice constants of Pt and Pd is small (only 0.8%), it may generate a very small compressive strain. This suggests that in the function of the Pt/Pd electrodes for glycerol oxidation, ligand effect and strain effect are very limited. On the other hand, through density functional theory calculations, Li et al. [33] concluded that in PtPd/C catalysts, the Pt atom bears negative charge while Pd atom is positively charged. (ii) Reaction route and extent of glycerol oxidation. Glycerol is a polyol and electrocatalytic oxidation of glycerol takes place through parallel and consecutive oxidation routes [9–11,17]. Therefore, not only the rate of adsorption and reaction of glycerol and OH⁻ but also the route and extent of glycerol oxidation on the different electrodes affect reaction current. Though no much difference in the reaction route and product of glycerol oxidation on Pt and Pd electrodes in alkaline solution was reported [9,17], the possibility of the difference in the route and extent of glycerol oxidation on the Pt-modified Pd electrodes from those on Pt and Pd electrodes can not be excluded.

Considering the important role of the amount of the deposited Pt in the activity of the Pt/Pd electrodes, the current density of the CVs of the Pt/Pd electrodes in Fig. 3a and b is normalized to per unit mass of Pt, and the results are presented in Fig. 3c. The sequence of the Pt mass specific peak current densities is Pt_(20s)/Pd > Pt_(10s)/Pd > Pt_(5s)/Pd > Pt_(30s)/Pd > Pt_(40s)/Pd. High peak current densities are obtained by the Pt_(5s)/Pd, Pt_(10s)/Pd and Pt_(20s)/Pd electrodes, with the peak current density on the Pt_(20s)/Pd electrode being several times higher than that on the Pt_(40s)/Pd electrode. However, the data related to the current density in Fig. 3c should be used with care, since not only the deposited Pt but also the Pd substrate can act as active sites to contribute to current density. Useful information about this can be obtained from the CVs themselves in Fig. 3c. The higher Pt mass specific peak current density on the Pt_(20s)/Pd electrode than that on the Pt_(5s)/Pd and Pt_(10s)/Pd electrodes suggests that in the function of the Pt/Pd electrodes Pd acts not only as promoting sites, by adsorbing OH⁻ and forming of Pd–OH_{ad}, but also as active sites to adsorb and oxidize glycerol. If Pt alone acts as active sites while Pd just acts as promoting sites, the Pt mass specific peak current density on the Pt/Pd electrodes should be gradually decreased with increasing Pt loading, since the formation of the Pt nanoparticles brings down the utilization of Pt due to that the Pt atoms under the particle surface are not available as active sites for glycerol oxidation.

4. CONCLUSIONS

The surface modification of polycrystalline Pd electrodes with Pt is conducted potentiostatically using chloroplatinic acid as the precursor of Pt. SEM images show that the Pd substrates are partially covered by the Pt nanoparticles of different sizes and the distribution of the Pt nanoparticles gets denser with increasing Pt loading. The electrocatalytic behavior of the Pt/Pd electrodes during glycerol oxidation in alkaline solution reveals that the activity of the electrodes strongly depends on the amount of Pt. In a wide range of the Pt loadings, the Pt/Pd electrodes show more negative oxidation potential and considerably higher peak current density than Pd and Pt electrodes. The Pt modification is found to be effective for improving the activity of Pd electrode towards glycerol oxidation.

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