

High Catalytic Activity of Pt-Modified Ag Electrodes for Oxidation of Glycerol and Allyl Alcohol

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The platinum modification of polycrystalline Ag electrode and the electrocatalytic oxidation of glycerol and allyl alcohol on Pt-modified Ag electrodes in alkaline solution have been investigated. Pt-modified Ag electrodes with different platinum loadings were prepared potentiostatically by using chloroplatinic acid as platinum precursor. Scanning electron microscope images indicate that platinum particles of different shapes and sizes are formed and the silver substrates are not fully covered by the deposited platinum. Cyclic voltammetric measurements reveal opposite catalytic behaviors of Ag and Pt electrodes and significantly enhanced catalytic activity of Pt-modified Ag electrodes in the oxidation of glycerol and allyl alcohol. In the both oxidation reactions, an increase and then a decrease of peak current with increasing platinum loading of the Pt-modified Ag electrodes are observed, showing a strong impact of the quantity of the deposited platinum on the catalytic activity of the Pt-modified Ag electrodes.

Keywords: Surface modification; Electrodeposition; Electrocatalytic oxidation; Glycerol; Allyl alcohol

1. INTRODUCTION

Great effort has been made to improve electrochemical properties like catalytic activity and anti-poisoning ability of metal electrodes, and bimetallic nanoparticulate electrodes have been of special interest, since this kind of electrodes can show enhanced catalytic activity and stability in electrochemical reactions, such as PtRu electrocatalysts for methanol oxidation [1,2]. Metal electrodes modified by other metals are also attractive. A review article by Spendelow et al. [3] summarized the improvement in catalytic activity of Pt electrode by ruthenium modification for the oxidation of carbon monoxide and methanol. Surface modification of substrate metal with a second metal can be performed by the methods like electrochemical deposition, chemical deposition, spontaneous

deposition, and physical vapor deposition. Electrochemical deposition is a versatile technique, by which a thin desired metal overlayer can be obtained on the surface of substrate metal through simple electrolysis of an aqueous solution containing the desired metal ion or its complex. Underpotential deposition and overpotential deposition, through the processes like potentiostatic deposition, linear sweep voltametric deposition, repeated potential cycling deposition, and galvanostatic deposition, are widely used electrochemical modification methods.

The modification of different kinds of platinum substrates with other metals has been investigated widely, such as Ru, Cu, Ag, Bi, Pb and Pd deposition on Pt(*hkl*) (*hkl* denotes planes orthogonal to the reciprocal lattice vector) [3,4] and Ag deposition on polycrystalline Pt substrates [5]. Platinum can also be used as modification metal, and surface modification of other metals with platinum has been investigated intensively, especially the platinum modification of gold. The modifications of different kinds of gold substrates, such as single crystal, polycrystalline, nanoparticles and nanorods of gold, with various forms of platinum like submonolayer, monolayer, multilayer and nanoparticles, by using modification methods like redox replacement by Pt of a Cu UPD monolayer on Au [6], chemical deposition [7], spontaneous deposition [8], electrochemical deposition [9], and physical vapor deposition [10], have been reported. Silver can also be used as modification metal and substrate metal. For example, Ag modification of Au(*hkl*) and Pt(*hkl*), and Pb, Tl and Bi modification of Ag(*hkl*) [4].

Silver is attractive as a potential replacement of platinum as an alkaline ORR (oxygen reduction reaction) cathode material due to its reasonably high activity and low cost [11], but it shows low catalytic activity for the electrocatalytic oxidation of alcohols like methanol, ethylene glycol and glycerol [12,13]. Silver can also be used as a second metal in the preparation of bimetallic nanoparticles, and improved catalytic activity of AgM (M: metal) nanoparticulate electrodes for the oxidation of alcohols has been reported, such as AgPt/C electrocatalysts for the oxidation of methanol [14,15] and AgPd/C electrocatalysts for the oxidation of methanol [16] and ethanol [17,18]. On the other hand, though the preparation and structure analysis of Ag-modified M electrodes and M-modified Ag electrodes have been investigated widely [4], the reports on catalytic activities of these kind of electrodes, such as the oxidation of glucose on Ag-modified Au(111) electrode [19] and the evolution and oxidation of hydrogen on Pt-modified Ag(111) electrodes prepared by means of physical vapor deposition and electrochemical potentiostatic deposition [20], are very limited. The preparation of Ag_{core}-Pt_{shell} nanoparticles by the successive chemical reduction method using reducing agents like sodium borohydride, sodium citrate and ethylene glycol and the electrocatalytic reduction of oxygen on Ag_{core}-Pt_{shell} nanoparticulate electrodes were reported as well [21,22]. We have recently reported on catalytic activity of Ag-modified Pd electrodes for allyl alcohol oxidation [23]. The electrochemical properties of Ag-modified M electrodes and M-modified Ag electrodes need further investigation.

Electrochemical modification method is not only very effective but also environmentally friendly. In this article, we report on surface modification of polycrystalline Ag electrode with platinum and electrocatalytic activity of Pt-modified Ag electrodes for the oxidation of glycerol (propane-1,2,3-triol) and allyl alcohol (2-propenol). The behaviors of Ag and Pt electrodes in the oxidation of glycerol and allyl alcohol, the enhanced catalytic activity of the Pt-modified Ag

electrodes, and the impact of the quantity of the deposited platinum on the behavior of the Pt-modified Ag electrodes, have been investigated.

2. EXPERIMENTAL

Electrochemical experiments were performed in a conventional single compartment three-electrode glass cell at room temperature (about 25 °C) using a LK98BII (Lanlike Ltd, China) electrochemical analyzer. Polycrystalline Ag and Pt disks of 4 mm in diameter embedded in PTFE were polished with alumina and cleaned ultrasonically in twice distilled water before use. A Pt coil and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively, in both surface modification and alcohol oxidation. The platinum modification of Ag electrode was carried out in a 0.05 mol L⁻¹ H₂SO₄ solution containing 1 mmol L⁻¹ H₂PtCl₆ by potentiostatic deposition of platinum at +0.20 V vs. SCE. Pt-modified Ag electrodes with different platinum loadings were prepared by changing the deposition time. In this article, these electrodes are denoted as Pt_(x)/Ag in which *x* represents the platinum deposition time.

Electrocatalytic oxidation of glycerol and allyl alcohol, respectively, on Ag, Pt and Pt/Ag electrodes was conducted through cyclic voltammetric (CV) method in a 0.5 mol L⁻¹ NaOH solution containing 0.1 mol L⁻¹ allyl alcohol or glycerol. The CV measurements were performed between -0.80 and +0.60 V in the first cycle, then the upper limit of the sweep was set at +0.20 V, and the CV curves in this potential region are used in this article. All potentials are reported with respect to SCE, except as specifically indicated.

3. RESULTS AND DISCUSSION

3.1. Platinum modification of Ag electrode

One of the advantages of electrochemical surface modification is that overlayer thickness or particle size of second metal can be well controlled. The coverage and structure of second metal adatoms deposited on substrate metal are closely related to the deposition method, condition and parameters. For potentiostatic deposition of platinum on silver substrates under a certain reaction condition (potential, concentration, temperature, pH etc.), the quantity of the deposited platinum is dependent on the deposition time; the longer the deposition time, the more the platinum loading. The deposition time of 5, 10, 20, 30 and 40 s were chosen in the experiments, and integrated charges obtained from these deposition processes were ca. 93, 190, 340, 450 and 620 μC, respectively, corresponding to 0.05, 0.10, 0.17, 0.23 and 0.31 μg of platinum loadings on the silver substrates (*d* = 4 mm), assuming a 100% of current efficiency. No formation of hydrogen bubbles on the silver substrates was observed during the platinum deposition. Since the deposition potential of +0.20 V is more negative than the Nernst potential for the same solution, the deposition process is overpotential deposition.

Fig. 1 shows scanning electron microscope (SEM) images of the Pt/Ag electrodes prepared by the different time of the platinum deposition. It is seen that platinum particles of different shapes and sizes are formed on the silver substrates and the size and coverage of the platinum particles are growing larger with the deposition time becoming longer. This indicates three-dimensional deposition of platinum. At the same time, it seems that the surfaces of the silver substrates are not fully covered by platinum, though it is difficult solely on the basis of the above SEM images to rule out the possibility of the formation of Pt monolayer (ML) on the silver surfaces, due to the low resolution of the images. But, as can be seen below, electrochemical behaviors of the Pt/Ag electrodes further confirm the existence of the uncovered silver surface domains. Waibel et al. [9] reported that about 0.2 V overpotential is required for electrochemical deposition of platinum on Au(111) and Au(100) single crystal substrates from an acidic electrolyte containing K_2PtCl_4 and the formation of three-dimensional clusters of platinum. Based on the results of electroreflectance, Tölle et al. [20] reported that physical vapor deposition of platinum on Ag(111) does not lead to a homogeneous platinum coverage, with the electrolyte having contact with the Ag(111) substrate even after coating with an average of 10 ML platinum, and that for electrochemically prepared Pt/Ag(111), the conspicuous structure of Ag(111) is obvious at an average coverage of 2 ML platinum but is nearly lost at an average coverage of 10 ML platinum.

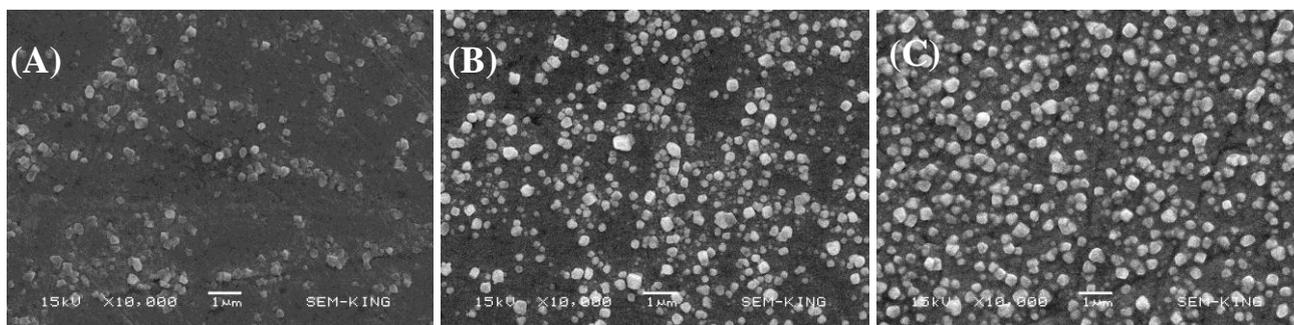


Figure 1. SEM images of Pt-modified Ag electrodes prepared by the platinum deposition time of 10 s (A), 20 s (B), and 40 s (C).

3.2 Glycerol oxidation on Ag, Pt and Pt/Ag electrodes

Fig. 2 shows cyclic voltammograms of Ag, Pt and Pt/Ag electrodes in a 0.5 mol L^{-1} NaOH solution containing 0.1 mol L^{-1} glycerol. In Fig. 2A, a peak at ca. -0.17 V with peak current of 4.3 mA cm^{-2} is observed for the Pt electrode. Glycerol oxidation on Pt electrode shows significantly low peak current compared to that on Au electrode in alkaline solution [24]. No distinct peak is observed for the Ag electrode in Fig. 2A, indicating no catalytic activity of the Ag electrode in this potential region. Glycerol oxidation on Ag electrode in alkaline solution takes place in the potential region of silver oxide formation, and AgO acts as the main active sites [12,13]. On the other hand, the CV curve of Pt_(20s)/Ag electrode shows a peak at ca. 0 V with peak current of 18.0 mA cm^{-2} , and onset oxidation potential on Pt_(20s)/Ag electrode is much more negative than that on Pt electrode. Significantly higher

catalytic activity of Pt_(20s)/Ag electrode than that of Ag and Pt electrodes can be seen from Fig. 2A. In Fig. 2B, showing catalytic activity of the Pt/Ag electrodes with different platinum loadings, the order of Pt_(20s)/Ag > Pt_(30s)/Ag > Pt_(40s)/Ag ≈ Pt_(10s)/Ag > Pt_(5s)/Ag in terms of peak current on these electrodes is observed, displaying an increase and then a decrease of peak current with increasing platinum loading of the Pt/Ag electrodes, while the peak current on Pt_(5s)/Ag electrode is a little higher than that on Pt electrode. Furthermore, very low peaks in the reverse sweep are observed for the Pt/Ag electrodes, indicating high poisoning resistance of the electrodes. Relatively high peaks in the reverse sweep were observed during glycerol oxidation on PtRu and PtSn electrocatalysts in alkaline solution [25]. Another feature of the CV curves of the Pt/Ag electrodes is that the oxidation peaks are not in good shape, showing a slow increase of current from -0.60 to 0 V in the positive sweep. No peak could be further resolved in this potential region even at a low sweep rate.

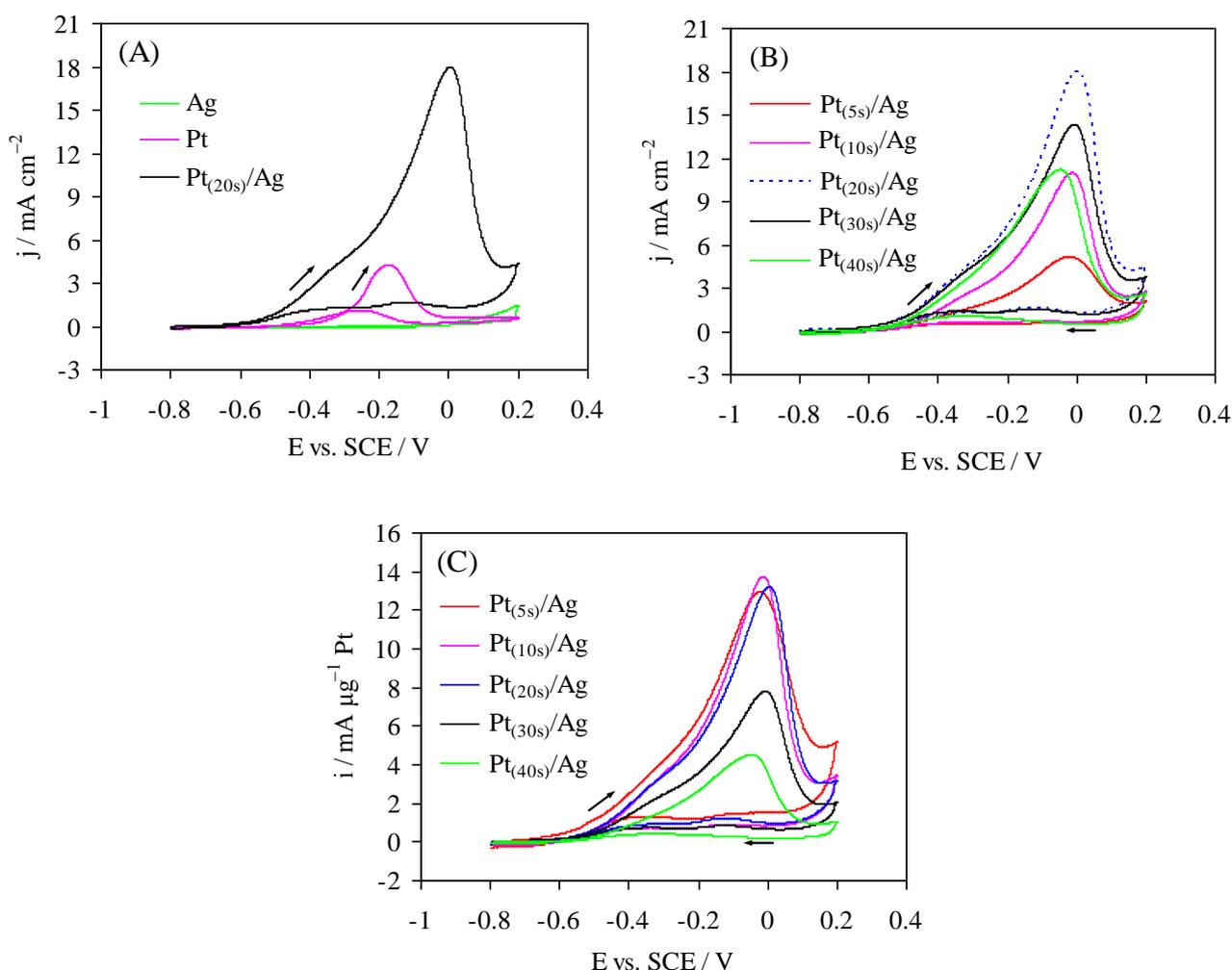


Figure 2. Cyclic voltammograms of Ag, Pt and Pt-modified Ag electrodes in 0.5 mol L⁻¹ NaOH containing 0.1 mol L⁻¹ glycerol. Currents are normalized to geometric area in (A) and (B) and to per unit mass of platinum loading in (C). Scan rate: 50 mV s⁻¹.

Taking into account of the catalytic activity of the Pt electrode and no catalytic activity of the Ag electrode as well as the behavior of the Pt/Ag electrodes with different platinum loadings, it is reasonable to conclude that the catalytic activity of the Pt/Ag electrodes is related to both platinum and silver, and platinum acts as the main active metal and silver acts as the promoting metal. The difference in the CV curves of Pt and Pt/Ag electrodes reveals the impact of silver substrate on the catalytic activity of the deposited platinum. For further investigation of the interaction between silver substrate and the deposited platinum, Pt and glassy carbon (GC) electrodes were also used as substrates, and Pt-deposited Pt electrodes and Pt-deposited GC electrodes were prepared by depositing platinum of equal amounts of the platinum loadings of the Pt/Ag electrodes. No significant difference was observed for glycerol oxidation on the Pt-deposited Pt electrodes compared to that on bare Pt electrode. For example, peak current of 4.6 mA cm^{-2} on a Pt-deposited Pt electrode with the platinum loading being close to that of Pt₍₂₀₎/Ag electrode was obtained under the same reaction condition as that shown in Fig. 2, which is about 7% higher than that on Pt electrode. This is considered due to the increase of platinum surface caused by the deposition of platinum. However, the 7% increase of peak current is not a significant one, considering the peak current of 18.0 mA cm^{-2} on Pt_(20s)/Ag electrode. On the other hand, no peak was observed for glycerol oxidation on the Pt-deposited GC electrodes. Therefore, it can be concluded that high peak current on Pt_(20s)/Ag electrode is mainly due to the influence of the silver substrate on the deposited platinum.

In Figs. 2A and B, the CV curves are normalized to geometric area of the Pt/Ag electrodes, which is convenient to show the variation in catalytic activity of the Pt/Ag electrodes with the change of the platinum loading. Since platinum acts as the main active sites, the CV curves of the Pt/Ag electrodes in Fig. 2B are normalized to per unit mass of the platinum loading, and the results are shown in Fig. 2C. It is seen that peak currents on Pt_(5s)/Ag, Pt_(10s)/Ag and Pt_(20s)/Ag electrodes are close to one another and are higher than that on Pt_(30s)/Ag and Pt_(40s)/Ag electrodes. With increasing platinum loading, more platinum atoms can not be used as active sites, which results in a lower utilization of platinum. When a large quantity of platinum is deposited, the behavior of the Pt/Ag electrodes will get close to that of Pt electrode.

The improved catalytic activity of the Pt/Ag electrodes can be attributed to bifunctional effect between platinum and silver. That is, glycerol is adsorbed and oxidized on platinum active sites and silver is to supply adsorbed oxygen-containing species like Ag–OH_{ads} and Ag₂O–OH_{ads} to oxidize carbonaceous adsorbates on the platinum sites. The underpotential oxidation of silver, the formation of the monolayer and multilayer of Ag₂O and the oxidation of Ag₂O to AgO with the positive sweep of Ag electrode in alkaline solution have been reported [13,26]. The formation of the electrochemisorbed OH_{ads} and O_{ads} species on the surface of Ag electrode with the positive sweep from -0.8 to $+0.2$ V vs. Hg/HgO in alkaline solution has also been reported [27].

3.3. Allyl alcohol oxidation on Ag, Pt and Pt/Ag electrodes

Fig. 3 shows CV curves of Ag, Pt and Pt/Ag electrodes in a 0.5 mol L^{-1} NaOH solution containing 0.1 mol L^{-1} allyl alcohol. In Fig. 3A, a low peak at -0.30 V with peak current of 2.1 mA

cm^{-2} on Ag electrode and a high peak at -0.11 V with peak current of 17.2 mA cm^{-2} on $\text{Pt}_{(20\text{s})}/\text{Ag}$ electrode are observed, respectively. Onset oxidation potentials for the two electrodes are close to each other, but the difference in peak current is about 8.2 times, revealing significantly high catalytic activity of the $\text{Pt}_{(20\text{s})}/\text{Ag}$ electrode. On the other hand, no distinct peak is observed for Pt electrode, indicating no catalytic activity of the Pt electrode for allyl alcohol oxidation. In Fig. 3B, showing catalytic activity of the Pt/Ag electrodes with different platinum loadings, peak currents display an increase and then a decrease with increasing platinum loading of the Pt/Ag electrodes, and the order of the peak currents is similar to that observed in glycerol oxidation. The Pt-deposited Pt electrodes and Pt-deposited GC electrodes mentioned in the Section 3.2 were also used in allyl alcohol oxidation. Similar peaks to that on bare Pt electrode were observed for the Pt-deposited Pt electrodes, and no peak was observed for the Pt-deposited GC electrodes.

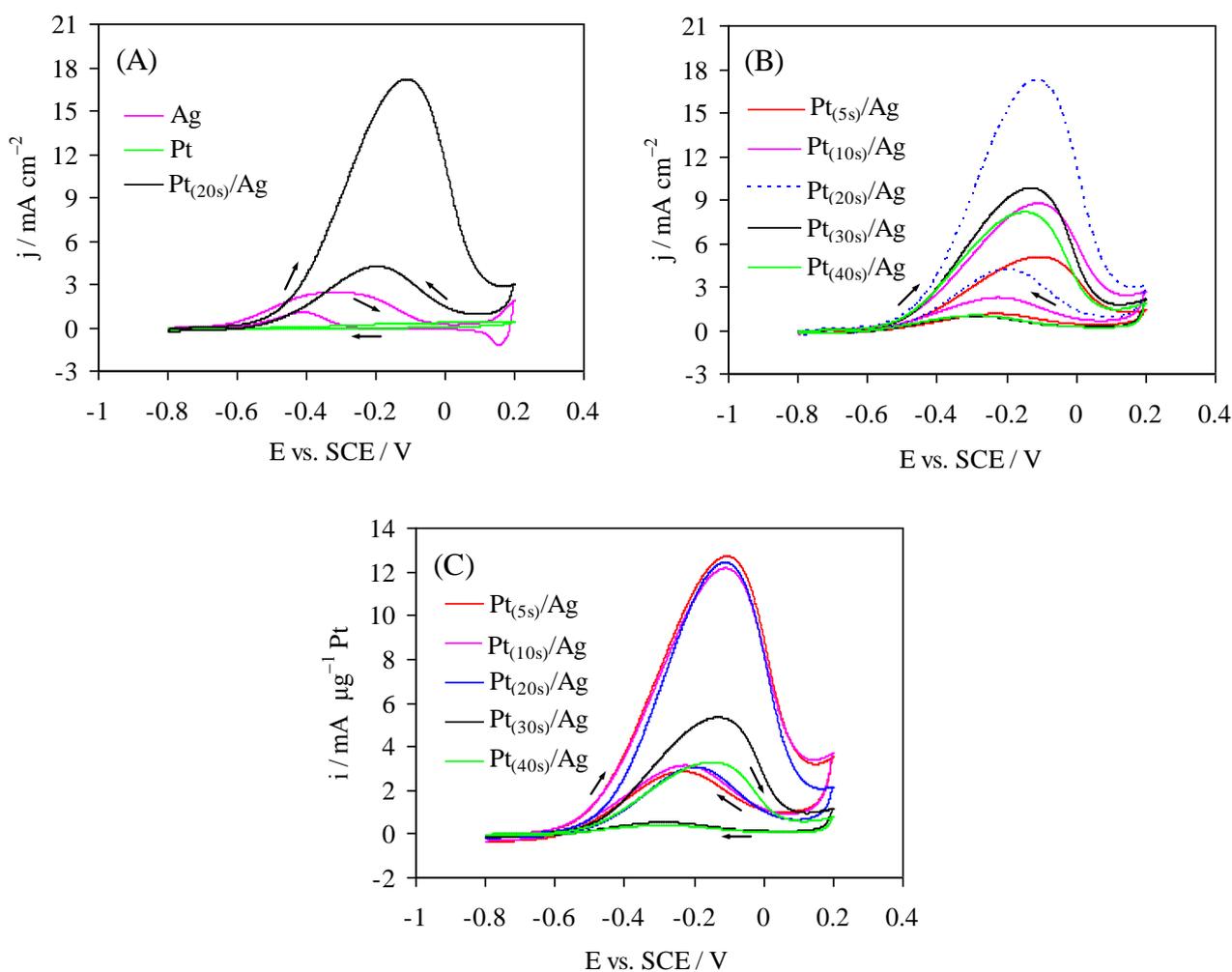


Figure 3. Cyclic voltammograms of Ag, Pt and Pt-modified Ag electrodes in 0.5 mol L^{-1} NaOH containing 0.1 mol L^{-1} allyl alcohol. Currents are normalized to geometric area in (A) and (B) and to per unit mass of platinum loading in (C). Scan rate: 50 mV s^{-1} .

A comparison of the CV curves of Ag and Pt/Ag electrodes reveals the difference in the catalytic activity of the two kinds of electrodes, caused by the surface modification of Ag electrode with platinum. It is seen that the peak currents on the Pt/Ag electrodes are higher than that on the Ag electrode, regardless of the platinum loadings of the Pt/Ag electrodes. For example, peak current on Pt_(5s)/Ag electrode is about 2.5 times as high as that on Ag electrode, though the platinum loading of Pt_(5s)/Ag electrode is quite low. Higher catalytic activity of the Pt/Ag electrodes than that of Ag and Pt electrodes can be clearly seen from Figs. 3A and B. These results also suggest that the silver substrates of the Pt/Ag electrodes are not fully covered by the deposited platinum. Considering no catalytic activity of the Pt electrode, the peak on the Pt/Ag electrode with a higher silver loading like Pt_(40s)/Ag should be much lower if the silver substrate is fully covered by platinum overlayer.

A point worth of discussion is the function mechanism of the Pt/Ag electrodes in allyl alcohol oxidation. Taking into account no catalytic activity of Pt electrode, low catalytic activity of Ag electrode and enhanced catalytic activity of Pt/Ag electrodes, one can think of the possibility that in the function of the Pt/Ag electrodes silver acts as the main active metal and platinum acts as the promoting metal. However, this contradicts with the function mechanism of the Pt/Ag electrodes in glycerol oxidation. Furthermore, a same order of the Pt/Ag electrodes with different platinum loadings in terms of peak current on them is observed in both glycerol oxidation and allyl alcohol oxidation. Accordingly, there is another possibility that in allyl alcohol oxidation on the Pt/Ag electrodes platinum acts as the main active metal and silver acts as the promoting metal. We believe that this mechanism is the actual one, and the reason is explained as follows: Both allyl alcohol and propan-1-ol are C₃ primary alcohols, and the difference in the molecular structure of allyl alcohol from that of propan-1-ol is C=C bond. Considering catalytic activity of Pt electrode for propan-1-ol oxidation [28], it is reasonable to conclude that no distinct catalytic activity of Pt electrode for allyl alcohol oxidation is due to the adsorption of C=C bond in the molecular chain of allyl alcohol and intermediates of the oxidation on the platinum surface, which makes the formation of Pt-OH_{ads} difficult, so further reaction is suppressed. In allyl alcohol oxidation on the Pt/Ag electrodes, on the other hand, Ag-OH_{ads} and Ag₂O-OH_{ads} formed on the silver substrates can react with allyl alcohol molecules adsorbed on the deposited platinum, so oxidation takes place and peak current increases with increasing platinum loading. With further increasing platinum loading, platinum particles are growing larger and new platinum particles are formed, while the silver surface is decreased. As a result, oxygen-containing species adsorbed on the silver substrates are decreased. Therefore, the interaction between allyl alcohol and intermediates adsorbed on the platinum particles and oxygen-containing species adsorbed on the silver substrates becomes difficult, which results in a low catalytic activity of the Pt/Ag electrodes with high platinum loadings. The detailed function mechanism of the Pt/Ag electrodes in allyl alcohol oxidation needs further investigation.

Based on the above discussion, the CV curves of the Pt/Ag electrodes in Fig. 3B are also normalized to per unit mass of the platinum loading, and the results are shown in Fig. 3C. Peak currents on Pt_(5s)/Ag, Pt_(10s)/Ag and Pt_(20s)/Ag electrodes are close to one another and are higher than that on Pt_(30s)/Ag and Pt_(40s)/Ag electrodes, which is similar to that shown in Fig. 2C.

Interesting behaviors of Ag, Pt and Pt/Ag electrodes can be found from Figs. 2 and 3: (i) Ag electrode shows catalytic activity for allyl alcohol oxidation but no catalytic activity for glycerol

oxidation. In contrast, Pt electrode shows catalytic activity for glycerol oxidation but no catalytic activity for allyl alcohol oxidation. (ii) In both oxidation reactions, Pt/Ag electrodes show enhanced catalytic activity and a similar variation in catalytic activity with the change of the platinum loading: peak current first increase and then decrease as the platinum loading is increased. The Pt/Ag electrodes with appropriate quantities of the platinum loading show significantly higher catalytic activity than Ag and Pt electrodes, indicating that the surface modification of Ag electrode with platinum is very effective for electrocatalytic oxidation of glycerol and allyl alcohol.

4. CONCLUSIONS

The Pt-modified Ag electrodes with different platinum loadings were prepared by means of potentiostatic deposition of platinum on polycrystalline silver substrates. The platinum deposition proceeded three-dimensionally and platinum particles of different shapes and sizes were formed on the silver substrates. Electrocatalytic oxidation of glycerol and allyl alcohol on Ag, Pt and Pt/Ag electrodes shows improved catalytic activity of the Pt/Ag electrodes. The catalytic activity of the Pt/Ag electrodes is dependent on both silver and platinum and is greatly affected by the quantity of the deposited platinum. With increasing platinum loading of the Pt/Ag electrodes, an increase and then a decrease of peak current are observed in the both oxidation reactions. The Pt/Ag electrodes with appropriate quantities of the platinum loading show significantly enhanced catalytic activity.

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