Direct Oxidation of Methanol on Self-Supported Nanoporous Gold Film Electrodes with High Catalytic Activity and Stability

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The electrocatalytic oxidation of methanol using precious metal catalysts has attracted great interest in fuel cells.[1–3] Precious metal platinum is commonly employed as the anode material for electrocatalytic oxidation of methanol in direct methanol fuel cells (DMFCs).[4,5] The electro-oxidation of methanol on Pt is complicated because of generation of strongly chemisorbed reaction intermediates from oxidation of methanol itself. Various species such as CO,[6,7] COH,[8,9] and HCO[10] have been suggested as intermediates. They often poison Pt or Pt-based catalyst during the electro-oxidation of methanol.[11] To avoid this poisoning, researchers have extensively used bimetallic multicomponent catalysts, such as Pt−Ru, Pt−Pd, and Pt−Au.[12–15]

Besides platinum, gold electrode is also used as a catalyst toward methanol oxidation in alkaline solutions, which can avoid the generation of the poisoning intermediates.[5] However, the polished gold electrode with smooth surface is a poor catalyst for methanol oxidation. It is known that rough, activated noble metals exhibit some unexpected properties in comparison with the counterparts with smooth surfaces in most cases. For example, gold electrode obtained with special methods possessed surprisingly high electrocatalytic activity.[16] These methods include thermal treatment approach, spontaneous formation, underpotential deposition, and successive reduction process.[17] In these methods, the gold electrodes were often fabricated by depositing Au nanoparticles onto foreign substrates, which might cause the electrodes to be unstable. Meanwhile, the electrocatalytic activities of these Au-nanoparticle-supported electrodes depend on the roughness factor (the ratio between the real surface area and the geometrical area of electrode) and the existence of special binding sites on the surface of the particles.[18] Their low roughness and slow electron transport limit their catalytic performance. Compared with the gold-nanoparticle-supported electrode, the gold electrode with nanoporous structure possessed much higher roughness and better electron transport, which led to distinguished performance in the analysis of trace ions.[19]

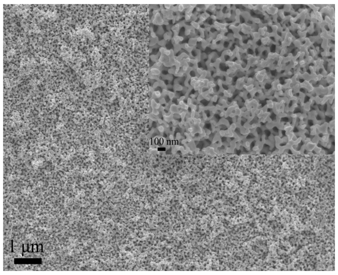

Figure 1. FESEM image of gold electrode after 30 cycles of alloying/dealloying in $ZnCl_2$/BA electrolyte at 120 °C. The inset is the enlarged image.

In this communication, we report that a novel self-supported nanoporous gold film (NPGF) electrode can be used for a highly effective direct electro-oxidation of methanol in alkaline solution at room temperature. This self-supported nanoporous gold film electrode was fabricated through multicyclic electrochemical alloying/dealloying of a polished gold electrode in an electrolyte composed of $ZnCl_2$ and benzyl alcohol (BA).[20] The activity of NPGF was about 400 times of that of the smooth gold electrode and did not decrease after 100 cycles of activity test.

Figure 1 shows the field-emission scanning electron microscope (FESEM) images of gold electrode after 30 cycles of alloying/dealloying in $ZnCl_2$/BA electrolyte at 120 °C. The gold electrode surface turned dark. A well-defined three-dimensional nanoporous structure was observed on the electrodes. The ligament and pore size of the gold electrode were about 60 and 100 nm, respectively. The roughness factor of NPGF electrode after 30 times of cycles was estimated to be as high as 560, indicating its ultrahigh surface area (Figure S1, Supporting Information).

Figure 2A shows the typical cyclic voltammograms of the KOH solution containing 1.5 mol/L methanol recorded on the polished gold and NPGF electrodes. On the NPGF electrode, the onset potential of methanol oxidation occurred at −0.07 V. A large anodic current peak was observed at 0.235 V, representing the catalytic oxidation of methanol. The oxidation current density on the NPGF electrode was

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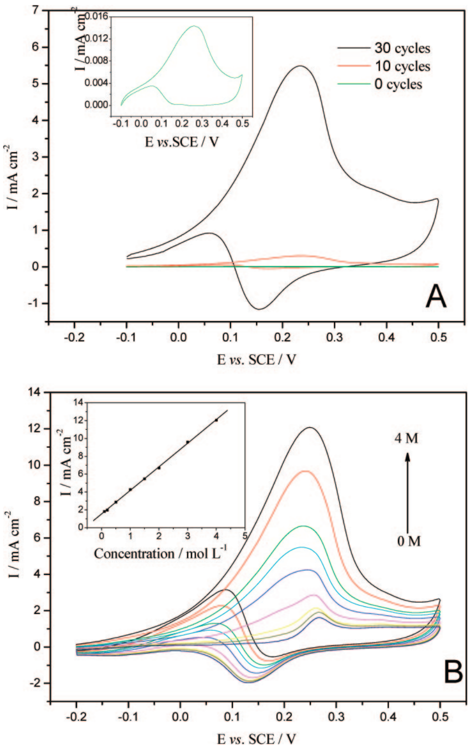

Figure 2. (A) CV curves recorded in 0.1 M KOH solution containing 1.5 mol/L methanol for the polished gold electrode and nanoporous gold electrodes. Scan rate: 20 mV s^{-1}. The inset picture was the magnified image of curve of the polished gold electrode. The nanoporous gold electrode was obtained after 10 and 30 cycles alloying/dealloying of gold electrode at 120 °C. (B) CV curves of 0, 0.1, 0.2, 0.5, 1, 1.5, 2, 3, and 4 mol/L methanol in 0.1 mol/L of KOH on NPGF, scan rate = 20 mV s^{-1}. The inset was the calibration plot of CV oxidation peak current density versus concentration of methanol.

5.96 mA cm^{-2}. This current density is much higher than those of polycrystalline gold electrode and nanoporous gold electrode obtained by dealloying of Au−Ag.[16,21] By the integration of charge consumed in the gold electrode, the activity of NPGF electrode was found to be about 400 times of that of the smooth gold electrode. Moreover, the current of oxidation peak of methanol increased a lot when the alloying/dealloying cycles of the nanoporous gold electrodes increased from 10 to 30. Therefore, it is concluded that cyclic alloying/dealloying method is an efficient way to fabricate three-dimensional nanoporous gold film with high activity to the oxidation of methanol and the high activity is attributed to the three-dimensional nanoporous structure.

In a methanol-free KOH solution, we observed an oxidation wave in the potential of 0.27 V, attributing to the formation of surface gold oxides (Figure S2, Supporting Information). According to Assiongbon,[5] OH^- anions were strongly adsorbed on Au electrodes in alkaline solutions. It is reasonable to associate the effect of methanol oxidation on Au electrodes with OH^- chemisorption. Therefore, we attribute the catalytic effect of NPFG electrode to the generated surface Au oxides and OH^- anions adsorbed on the surface of nanoporous Au. These OH^- anions are known to act as an electron-transfer mediator in the oxidation process.[22] Obviously, the nanoporous structure of the NPFG electrode greatly favors the formation of surface gold oxides and OH^- chemisorption.

Figure 2B shows the cyclic voltammograms of methanol with different concentrations in 0.1 mol/L KOH solution on the NPGF electrode. It can be seen that the oxidation peak current density increases with increasing methanol concentration in the solution, exhibiting a linear relationship (inset of Figure 2B). However, the oxidation peak potential of methanol shifts slightly. This is attributed to the influence of the formation of surface gold oxides. In the alkaline solutions containing methanol, the oxidation current arises from the oxidation of methanol, OH^- anions, and gold. During the oxidation of methanol in the alkaline solutions, plenty of OH^- anions were first strongly trapped by the NPGF electrode to assist the generation of abundant surface Au oxides.[5] Methanol could then be oxidized on these surface Au oxides at higher anodic potential scan, accompanied by reduction of part of the Au oxides to Au. The remaining surface Au oxides would be electrochemically reduced at cathodic potential scan, as revealed by the cathodic reduction peak in Figure 2B. Therefore, increasing the concentration of methanol resulted in a decrease in the remaining surface Au oxides, which led to the gradual decrease in the cathodic reduction peak.[18]

In Figure 3A, the oxidation peak current density increased accordingly with a scan rate increasing from 10 to 70 mV s^{-1}. The calibration plot (inset of Figure 3A) shows a good linear relationship between the oxidation peak current density and scan rate, indicating that the electrode reactions are surface-controlled processes. The ratio of anodic oxidation peak current density to cathodic reduction peak current density (I_{pa}/I_{pc}) decreased with increasing scan rate (Figure S3, Supporting Information), confirming that surface Au oxides contributed to the oxidation of methanol.[18]

The stability of the NPGF electrode, reflected by the oxidation peak current densities of methanol oxidation measured at different potential cycles, is shown in Figure 3B. In the initial CV curve, the oxidation peak current density was 5.96 mA cm^{-2}. After 100 potential cycles, the oxidation peak current density was 5.90 mA cm^{-2}, revealing no significant deactivation and an extremely high stability of the NPGF electrode. Therefore, our NPGF electrode can well-solve the gold electrode instability toward electrooxidation of methanol in the previous study.[16] This high stability is proposed to be attributed to plenty of active sites on the NPGF electrode. These active sites may strongly adsorb much OH^- anions and produce abundant surface Au oxides for the fast oxidation of methanol. To further understand the high stability of the nanoporous gold film, CV in 0.5 mol/L of H_2SO_4 solution was employed to compare the electrochemically active surface area of gold electrodes before and after 100 cycles of activity test in 0.1 mol/L of KOH solution containing 1.5 mol/L of methanol (Figure S4, Supporting Information). Almost no loss of redox activity was observed even after 100 cycles of activity test. Meanwhile, the FESEM image of gold electrodes further confirmed no obvious change for three-dimensional nanoporous structure of the NPGF electrode after 100 potential

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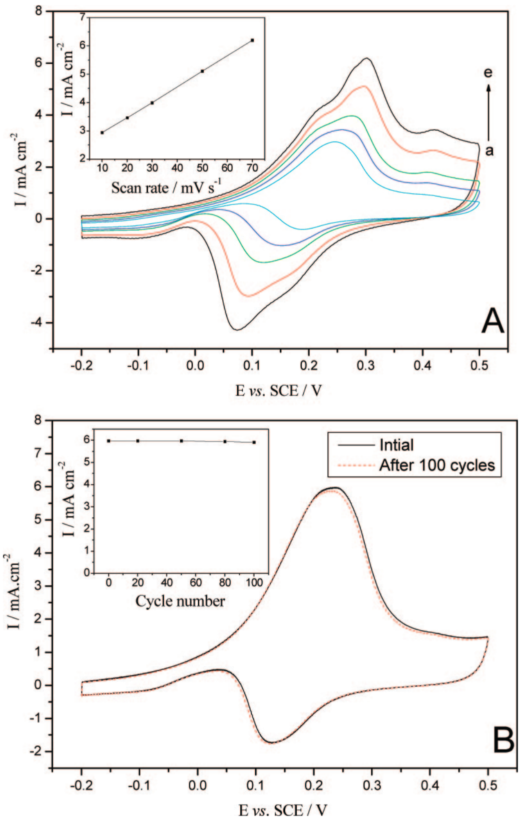

Figure 3. (A) CV curves of 1.5 mol/L methanol in 0.1 mol/L KOH solution on the NPGF electrode with different scan rates. Scan rate: (a) 10, (b) 20, (c) 30, (d) 50, and (e) 70 mV s^{-1}. The inset was the calibration plot of CV oxidation peak current density versus scan rate. (B) Initial and 100 potential cycle CV curves of 1.5 M methanol in 0.1 mol/L KOH on NPGF. Scan rate = 20 mV s^{-1}. The inset was the calibration plot of CV oxidation peak current density versus cyclic number.

cycles of activity test (Figure S5, Supporting Information), providing strong evidence for the high stability of our NPGF electrode. The high electrocatalytic activity and stability of NPGF electrode was further confirmed by the chronoamperometric technique (Figure S6, Supporting Information). As expected, the initial and limiting currents of NPGF electrode were much higher than those of the polished gold electrode during the test.

The overall conversion of methanol was analyzed by headspace gas chromatography with a flame ionization detector (Figure S7, Supporting Information). We found that the overall conversion of methanol was dependent on the electrocatalytic reaction time, which increased remarkably within 5 min and stablized at about 98% after 1 h, further confirming the high catalytic activity of the NPGF electrode.

In summary, we demonstrated that a novel self-supported NPGF electrode with ultrahigh surface area possessed high electrocatalytic activity and stability toward the direct oxidation of methanol. The high electrocatalytic activity and stability may be attributed to plenty of active sites on the NPGF electrode. The resulting NPGF electrode is very promising in the fields of direct methanol fuel cells, catalysis, sensor, and so on.

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Supporting Information Available: The preparation and characterization as well as electrocatalytic activity test procedures. CV curves of the polished gold and NPGF electrodes. Plot of the ratio of anodic oxidation peak current density to cathodic reducation peak current density versus scan rate for the NPGF electrode. CV curves recorded in 0.5 mol/L H_2SO_4 at NPGF, before and after 100 potential cycles of activity test. FESEM image of NPGF gold electrodes before and after 100 cycles of activity test. Chronoamperometries for methanol oxidation on the gold electrodes. The overall methanol conversion of methanol oxidation on the NPGF (PDF). The material is available free of charge via the Internet at http://pubs.acs.org.

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