Preparation of Nanoporous Pd/CuO by Dealloying and Their Electrocatalysis for Methanol in Alkaline Condition

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A novel and simple approach for fabrication of nanoporous Pd/CuO catalysts is reported. The nanoporous Pd/CuO catalysts were successfully prepared by chemical dealloying Ti-Cu-Pd amorphous alloy in a 1.25 M HCl solution. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) tests homogeneous nanoporous structures are formed. The Pd: CuO ratio of the catalysts could be controlled by adjusting the original composition of the alloy. Cyclic voltammetry (CV) and chronoamperometry (CA) were used to measure the electrocatalytic activities of the Pd/CuO catalysts. It was found that the catalytic activity was improved firstly and then depressed by increasing Pd content within both EASA and methanol electro-oxidation region. The catalyst prepared by Ti30Cu60Pd10 ribbon showed the best catalytic activity due to appropriate Pd: CuO ratio. The peak currents densities in the CV curves were increased with the increase of the methanol concentration, and the catalysts maintained good electrocatalytic activities in the solution with high methanol concentration (4 M). In addition, the charge transfer resistances tested by electrochemical impedance spectroscopy (EIS) decreases with the increase of CuO content, this indicates Pd: CuO ratio plays very important role in the electro-catalytic process and confirms the bifunctional mechanism of CuO.

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Small organic molecules have attracted intense attention as promising applications in fuel cell field. To date, Pt and Pt based catalysts are the most widely used catalysts in fuel cell anode for small organic molecules electro-oxidation. However, the commercial application of fuel cells is limited by the high cost and low stability of traditional Pt catalysts. Hence, it is important to develop new catalysts with low cost and high electrochemical activities. Pd is the most Pt-like material, and compared with Pt, Pd is less expensive. Moreover, Pd catalysts exhibit higher electro-catalytic perfromence and better CO resistance than Pt. However, the bulk Pd cannot meet the requirement of commercial application due to its relatively low catalytic activity. Adding auxiliary materials is a traditional way to enhance the catalytic activity of Pd. The foreign metal can improve the catalytic activity via electronic effect, such as Ni,3 Co,3 Fe3–5 and Ru.6 Moreover, noble metal catalysts usually suffer from catalysts poison induced by CO adsorption during the catalysis process. The oxygen-containing groups generate on transition metal oxides (such as CuO,7 TiO28 and WO3)9 can effectively remove CO, therefore the transition metal oxides is another common species of auxiliary materials. In order to maximize the utilization of Pd, it is necessary to synthesize catalysts with high specific surface area. Nanoporous materials have been drawn much attention for their wide applications such as sensing,10 catalysis,11,12 and fuel cells3,4,13 due to their large specific surface area, excellent electrical conductivities and high stability. Many efforts have been devoted to fabricate porous nanostructures, such as hydrothermal growth, template synthesis and chemical/electrochemical dealloying. Among these methods, dealloying stands out such as hydrothermal growth, template synthesis and chemical/ electrochemical dealloying. Among these methods, dealloying stands out because it is a simple and effective way to fabricate well defined 3D bicontinuous nanostructure.5 Dealloying is a selective dissolution process which less noble metal is removed from the alloy. A series of alloys are used as the dealloying precursor.14 The traditional products of dealloying process are pure or alloy metal, sponge-like transition metal oxides nanostructure prepared by dealloying method is rare. Here, we suggest the preparation of nanoporous Pd/CuO catalysts with controllable components in low Pd content via a simple dealloying process. We demonstrate the Pd/CuO ratio of catalysts with similar morphology can be controlled by tailoring the alloy composition. Moreover, these catalysts exhibit remarkable catalytic activity for methanol electro-oxidation in alkaline medium.

Experimental

Fabrication of the nanoporous Pd/CuO and Pd catalysts.— All chemicals were used as received without any further purification. The precursor Ti-Cu-Pd amorphous alloy was prepared by a melt spinning method which can be described as follows. Pure Ti, Cu and Pd were arc melted into alloy ingots in a titanium–gettered argon atmosphere for several times. Then the alloy ingots were remelted in quartz tubes and ejected onto a Cu wheel rotating. After that, the rapidly solidified Ti-Cu-Pd amorphous alloys were cut into 20 mm × 1.5 mm × 25 μm size for further processing. The nanoporous Pd/CuO materials were fabricated by selectively etching the amorphous alloy via chemical dealloying at 90 C in 1.25 M HCl solution for 5 h. After dealloying, the as-prepared Pd/CuO catalysts were washed in the deionized water and then dried in the room temperature. The fabrication of np-Pd catalyst was similar to Pd/CuO catalysts. The precursor Al-Pd amorphous alloy was prepared by a similar melt spinning method and was dealloyed in the 1.0 M NaOH solution for 24 h. After dealloying, the np-Pd catalyst was washed in the deionized water and dried in the room temperature.

Electrochemical evaluation of nanoporous Pd/CuO catalysts.— All the electrochemical measurements were carried out using Gamry Interface 1000 work station at room temperature. The tests were performed in a traditional three-electrode system which the Pd/CuO (or np-Pd) catalysts, platinum mesh electrode and SCE were served as the working electrode, counter electrode and the reference electrode, respectively. The electrochemical experiments for methanol electro-oxidation were recorded in 0.5 M NaOH solution with different concentration of methanol. The CV tests were carried out at a scanning rate of 25 mV/s from −0.3 V to 0.8 V. CA tests were proceeded at the peak potential of the methanol electro-oxidation in CV tests (−0.2 V). EIS measurements were performed at −0.2 V, amplitude was 10 mV, the initial and final frequencies of the EIS tests were 10000 Hz and 0.1 Hz, respectively. All the electrochemical tests were carried out at room temperature. The masses of Pd in samples which are used to normalize the current densities are measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Results and Discussion

Fig. 1 shows the surface morphology of nanoporous Pd/CuO catalysts prepared by Ti-Cu-Pd amorphous alloys with various Pd content. It is clearly observed that all the samples exhibit similar nano structure. The typical bicontinuous structure is formed, and both ligaments
Figure 1. SEM images of Pd/CuO catalysts prepared by Ti30Cu69Pd1 (a), Ti30Cu65Pd5 (b), Ti30Cu60Pd10 (c) and Ti30Cu50Pd20 (d) ribbon.

and nano pores connect together. The distribution of ligaments and pores are uniform and the sizes of both the ligaments and pores are approximately 15 nm. The SEM images indicates that the original composition of the ribbons have little effect on surface morphology. Dealloying process was carried out under free corrosion, Ti atoms were selectively dissolved, relative stable Pd and Cu atoms left behind and driven to assemble into 3D nanoporous structure via spinodal decomposition mechanism. Nano sized Cu is chemical active, therefore Cu is oxidized into CuO in the high reaction temperature.

Fig. 2 shows the TEM and HRTEM images of dealloyed Ti30Cu60Pd10 ribbon. The ligaments interconnect and mutually overlap, then exhibit sponge-like structure which is in agreement with SEM observation. The HRTEM image shows good crystallinity of as-prepared nanoporous catalyst. Different lattice parameters are observed in the ligaments. The d_{111} = 0.23 ± 0.01 nm and d_{200} = 0.22 ± 0.1 nm are correlate with the CuO (Fig. 2b), the angle labeled is 60.6° which is exactly correspond to the theoretical value of interfacial angle between the (111) and (100) planes. Another group of crystal planes with different orientation was shown in Fig. 2c, the plane angle is 56.5° and the interplanar spacings of the crystal planes are d_{200} = 0.20 ± 0.01 nm and d_{111} = 0.22 ± 0.01 nm, which are corresponding to metallic Pd. The elemental distribution in the porous structure is provided by TEM-EDX maps. It can be clearly seen that the signals of Pd and Cu and O cover all over the sample and in according with the catalyst shape. This phenomenon demonstrates that the distributions of these elements are homogeneous, no gathering occurs.

XPS spectra were performed to analyze the surface composition of the as-prepared catalysts. Fig. 3 shows the XPS spectra of Pd/CuO catalyst which fabricated by Ti-Cu-Pd amorphous alloy. Fig. 3a is the full spectrum of the sample, Ti signal can be seen in the spectrum which is attributed to Ti residual. Pd 3d spectrum (Fig. 3b) shows a doublet peak at 335.0 eV and 340.2 eV which are corresponding to Pd^{0} orbits. Pd 3d spectrum indicates that Pd would be stable and no PdO would be generated in the dealloying process. The Cu 2p spectrum is much complicated. It can be seen that the primary peak locates at 934.1 eV and the sub-peak locates at 953.7 eV, which are corresponding to the...
Figure 3. XPS spectra of Pd/CuO catalyst (a) and the detailed XPS spectra of Pd 3d (b) and Cu 2p (c).

Cu 2p3/2 and Cu 2p1/2 of the CuO, respectively. In addition, two intense satellite signals occur at 942.9 eV and 962.2 eV, which may be attributed to multielectron excitation and the satellite peaks is an obvious characteristic to recognize CuO among Cu0, Cu1+ and Cu2+.17 According to Cu 2p spectrum, Cu was oxidized completely during the etching.

Figure 4. CV curves in 0.5 M NaOH of pure np-Pd and Pd/CuO materials prepared by different compositions: Ti30Cu69Pd1, Ti30Cu65Pd5, Ti30Cu60Pd10 and Ti30Cu50Pd20.

The CuO: Pd ratio of the samples was examined by ICP-AES. As shown in Table I, the CuO: Pd ratio decreases with the increase of Pd content in original ribbon. In addition, the composition of the catalysts changed based on the original amorphous alloy, the Cu: Pd ratio of the catalysts decreased with the increasing of Pd in the original amorphous alloy. This indicates that Pd and Cu would be stable in the dealloying process.

As shown in Fig. 4, CV tests were used to record the electrochemical properties of the as-prepared catalysts in 0.5 M NaOH solution at a scan rate of 25 mV/s. According to the curves, the electrochemical features of all the catalysts are similar. Pd oxides were formed on the surface of the Pd/CuO catalysts at about −0.12 V during the positive scan and reduced at about −0.38 V during the negative scan. The EASA of the catalysts was calculated from the coulombic charge associated with Pd oxide reduction, according to the formula:

$$EASA = \frac{Q}{Q_{ref}} \cdot \frac{[Pd]}{\text{mass area}}$$

Here, $Q$ is the coulombic charges for Pd oxide reduction, $Q_{ref}$ is a constant of 424 μC/cm² and the [Pd] is mass area ratio of the catalysts. The EASA of the catalysts prepared by Ti30Cu69Pd1, Ti30Cu65Pd5, Ti30Cu60Pd10 and np-Pd catalyst are 15.55 m²/g, 19.27 m²/g, 6.39 m²/g and 9.37 m²/g, respectively. Few Pd active sites would be generated on catalyst surface prepared by Ti30Cu69Pd1 due to low Pd content. For high Pd content catalysts (prepared by Ti30Cu50Pd20), abundant Pd atom aggregate together which may be due to low surface diffusivity of Pd at the amorphous alloy/electrolyte interfaces, despite Pd is enough, Pd atom cannot expose to the surface, leading to insufficient utilization of Pd. The catalyst prepared by Ti30Cu60Pd10 possesses sufficient Pd content and appropriate surface diffusivity, therefore acquires the highest EASA value.

The methanol electro-oxidation activity of Pd/CuO catalysts was examined. Fig. 5 shows the CV curves of these electrocatalysts in 0.5 M NaOH + 1 M methanol solution at a scan rate of 25 mV/s. All the curves are normalized by the equivalent mass of Pd ($p^{equiv}$) and EASA ($EASA^{(equiv)}$), respectively. No methanol electro-oxidation peak occurs in the CV curve of the catalyst prepared by Ti30Cu69Pd1 ribbon (insert of Fig. 5a), indicates that the catalyst is insensitive for methanol oxidation. This is because of low Pd content in the catalysts. However, with the increase of Pd content, the catalysts exhibit catalytic activity towards methanol oxidation.

| Table I. Relative content of the samples prepared by different compositions. |
|----------------|----------------|----------------|----------------|----------------|
| Original ribbon | Ti30Cu69Pd1 | Ti30Cu65Pd5 | Ti30Cu60Pd10 | Ti30Cu50Pd20 |
| Cu: Pd ratio of samples | 68.1 | 18.2 | 4.0 | 2.2 |

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effect for the methanol electro-oxidation. As shown in Fig. 5, obvious methanol electro-oxidation peaks occur at about $-0.2\text{ V}$ in the forward scan. The peak current density is a key parameter to characterize the catalytic activity due to its magnitude is proportional to the amount of methanol oxidized on catalysts. The $j_{\text{mass}}$ of the sample made by Ti$_{30}$Cu$_{65}$Pd$_5$, Ti$_{30}$Cu$_{60}$Pd$_{10}$ and Ti$_{30}$Cu$_{50}$Pd$_{20}$ and pure np-Pd catalyst are 283.22 mA/mg, 577.85 mA/mg, 89.71 mA/mg and 54.09 mA/mg, respectively. The $j_{\text{EASA}}$ of the forward oxidation peaks of the catalysts prepared by Ti$_{30}$Cu$_{65}$Pd$_5$, Ti$_{30}$Cu$_{60}$Pd$_{10}$, Ti$_{30}$Cu$_{50}$Pd$_{20}$ and pure np-Pd catalyst are 1.82 mA/cm$^2$, 3.00 mA/cm$^2$, 1.69 mA/cm$^2$ and 0.44 mA/cm$^2$, respectively. Both the CV curves normalized by equivalent mass of Pd and EASA indicate that the electrocatalytic performance of the Pd/CuO catalysts are higher than that of the pure np-Pd catalyst. In addition, the catalyst prepared by Ti$_{30}$Cu$_{60}$Pd$_{10}$ amorphous alloy would exhibit the highest catalytic activity. The onset potential is defined as the potential where the inflection occurs on the CV curve. The onset potential is related to the electro-oxidation of methanol and its intermediate products. The onset potentials of the sample made by Ti$_{30}$Cu$_{65}$Pd$_5$, Ti$_{30}$Cu$_{60}$Pd$_{10}$, Ti$_{30}$Cu$_{50}$Pd$_{20}$ and pure np-Pd catalyst are about $-0.37\text{ V}$, $-0.40\text{ V}$, $-0.33\text{ V}$ and $-0.31\text{ V}$, respectively. More negative onset potential indicates that the over potential of methanol oxidation would become higher and electrocatalytic methanol oxidation would occur easier. According to the CV curves, the catalyst prepared by Ti$_{30}$Cu$_{65}$Pd$_{10}$ exhibits the best catalytic activity. Also, as shown in Table II, based on the different electrochemical parameters, the electro-oxidation activity of our Pd/CuO catalyst is compared to those reported in other literature, some improvements are shown as follows: 1) The peak potential of the methanol oxidation at the as-prepared Pd/CuO catalysts is lower than that of the pure np-Pd and PdNPs/PVP-graphene and catalysts, this phenomenon indicates that the methanol oxidation kinetics are improved by the addition of CuO. 2) The peak current densities of the Pd/CuO catalysts are higher than that of the pure np-Pd catalysts and comparable to the other catalyst with transition metal oxide catalysts, indicating that the addition of CuO can enhance the electrocatalytic activities of Pd catalysts. 3) Pt and Pt-based catalysts are the most common catalysts for methanol electro-oxidation, but Pt is too expensive. The electro-catalytic activities of Pd/CuO catalysts are comparable to the Pt catalysts. This method of preparation of the Pd/CuO catalysts provides a promising way to fabricate non-Pt catalysts.

CA tests were performed to confirm the results of CV. Fig. 6 shows the CA curves normalized by equivalent mass of Pd at the peak potential for methanol electro-oxidation in CV test ($-0.2\text{ V}$) in 0.5 M NaOH + 1 M methanol solution. All the curves exhibit relatively higher value at first stage due to the reaction substance adsorption on the Pd active sites, and then the curves tend to stability. The best catalytic activity is obtained for the nanoporous Pd/CuO

![Figure 5](image5.png)  
**Figure 5.** CV curves normalized by equivalent mass of Pd (a) and EASA (b) in 1 M CH$_3$OH and 0.5 M NaOH of pure np-Pd and nanoporous Pd/CuO catalysts prepared by different compositions: Ti$_{30}$Cu$_{65}$Pd$_5$, Ti$_{30}$Cu$_{60}$Pd$_{10}$ and Ti$_{30}$Cu$_{50}$Pd$_{20}$. The inset in (a) is CV curve for catalyst prepared by Ti$_{30}$Cu$_{69}$Pd$_1$ amorphous alloy.

![Figure 6](image6.png)  
**Figure 6.** CA curves normalized by equivalent mass of Pd in 1 M CH$_3$OH and 0.5 M NaOH of pure np-Pd and Pd/CuO materials prepared by different compositions: Ti$_{30}$Cu$_{65}$Pd$_5$, Ti$_{30}$Cu$_{60}$Pd$_{10}$ and Ti$_{30}$Cu$_{50}$Pd$_{20}$.

### Table II. Comparison of different electrode materials for methanol electro-oxidation.

| Electro catalyst | Electrolyte | Onset potential / V (vs SCE) | Peak potential / V (vs SCE) | Peak current density | Reference |
|-----------------|-------------|-----------------------------|-----------------------------|----------------------|-----------|
| np-Pd           | 0.5 M methanol + 1 M KOH | $-0.401$                     | $-0.042$                     | 223.52 mA/mg         | 18        |
| Pd/rGO/CFP      | 1.0 M methanol + 0.5 M NaOH | $-0.155$                     | $0.066$                      | 395.94 mA/mg         | 19        |
| PdNPs/PVP-graphene | 0.5 M methanol + 1 M NaOH | $-0.335$                     | $0.1$                       | 610 mA/mg           | 21        |
| PdCuSnCNTs      | 0.5 M methanol + 1.0 M KOH | $-0.481$                     | $0.1$                       | 432.02 mA/mg         | 22        |
| Pd/Fe3O4/GC     | 1.0 M methanol + 0.5 M NaOH | $-0.481$                     | $0.1$                       | 432.02 mA/mg         | 23        |
| Pt-CeO2/C       | 1.0 M methanol + 0.5 M H$_2$SO$_4$ | $-0.4$                      | $-0.19$                     | 1.33 mA/cm$^2$      | 24        |
| Pt/WO$_3$/MC    | 1.0 M methanol + 0.5 M NaOH | $-0.4$                      | $-0.19$                     | 1.33 mA/cm$^2$      | 25        |

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prepared by Ti$_{30}$Cu$_{60}$Pd$_{10}$ amorphous alloy, which is coincident with CV experiments.

According to the CV and CA tests, the reason for the variation tendency of catalytic activity may be explained by the bifunctional mechanism. The C–H and C–O bond should be broke when methanol electro-oxidation happens. The total reaction can be described as follows:26,27

\[
Pd + OH^- \rightarrow Pd-OH_{\text{ads}} + e^- \quad [2]
\]

\[
Pd + CH_3OH \rightarrow Pd-CH_3OH_{\text{ads}} \quad [3]
\]

\[
Pd-CH_3OH_{\text{ads}} + 4OH^- \rightarrow Pd-CO_{\text{ads}} + 4H_2O + 4e^- \quad [4]
\]

\[
Pd-OH_{\text{ads}} + Pd-CO_{\text{ads}} + 2OH^- \rightarrow 2Pd + CO_2 + H_2O \quad [5]
\]

\[
Pd + CH_3OH_{\text{ads}} \rightarrow Pd-CH_3OH_{\text{ads}} + 4OH^- \rightarrow Pd-CO_{\text{ads}} + 4H_2O + 4e^- \quad [4]
\]

\[
Pd-OH_{\text{ads}} + Pd-CO_{\text{ads}} + 2OH^- \rightarrow 2Pd + CO_2 + H_2O \quad [5]
\]

Due to the insufficient oxidation of methanol molecules, the intermediates, such as CO, would be generated and adsorbed on Pd surface, which is called catalyst poison. The intermediates adsorbing on the Pd surface would restrain the adsorption of methanol molecules. As a result, the methanol molecules electro-oxidation reaction would be depressed and the current density of methanol oxidation would decrease.

Cu$^{2+}$ species can serve as adsorption sites for oxygen-containing groups.28 These oxygen-containing groups can react with the intermediates generated on the surface of Pd active sites. In addition, the synergy effect between Pd and CuO would result in lower anodic over-potential due to the reduced potential value of the H$_2$O adsorption.7 Hence, the catalytic activity of Pd could be enhanced. The bifunctional mechanism of CuO was proposed as:29

\[
CuO + H_2O \rightarrow CuO - OH_{\text{ads}} + H^+ + e^- \quad [6]
\]

\[
CuO - OH_{\text{ads}} + Pd - CO_{\text{ads}} \rightarrow Pd + CuO + CO_2 + H^+ + e^- \quad [7]
\]

\[
Pd \ldots CuO(\text{interface}) + xCO \rightarrow Pd \ldots CuO_{1-x}(\text{interface}) + xCO_2 \quad [8]
\]

Due to the insufficient oxidation of methanol molecules, the intermediates, such as CO, would be generated and adsorbed on Pd surface, which is called catalyst poison. The intermediates adsorbing on the Pd surface would restrain the adsorption of methanol molecules. As a result, the methanol molecules electro-oxidation reaction would be depressed and the current density of methanol oxidation would decrease.

The CuO: Pd ratio is an important parameter for the catalysts. For the low Pd content samples, a small number of Pd active sites expose to the catalyst surface, hence the catalytic activities is low, such as the catalysts prepared by Ti$_{30}$Cu$_{60}$Pd$_{5}$. For the high Pd content sample, more Pd active sites were generated during the dealloying process. However, the CuO content would decrease due to the relative lower Cu content in the original alloy. Therefore the effect of bifunctional mechanism is impaired. The sample prepared by Ti$_{30}$Cu$_{60}$Pd$_{10}$ gains the balance between the amount of Pd active sites and CuO. This would improve the catalytic activity of the catalysts.

Fig. 7 represents the methanol concentration effect on the profile of CV curves for the as-prepared catalysts. The CV tests were performed in 0.5 M NaOH solution with adding different methanol.

\[\text{Figure 7. CV curves in 0.5 M NaOH and various methanol concentrations for samples prepared by different compositions: Ti}_{30}\text{Cu}_{60}\text{Pd}_{5} \ (a), \ Ti}_{30}\text{Cu}_{60}\text{Pd}_{10} \ (b) \text{ and Ti}_{30}\text{Cu}_{60}\text{Pd}_{20} \ (c). (d) The methanol concentration-peak current densities plot of the current density values of the methanol oxidation peaks at electrocatalysts prepared by different amorphous alloys in 0.5 M NaOH solution with the logarithm of methanol concentration.}\]
As shown in Fig. 8b, all curves of the samples exhibit similar shapes. Methanol concentration. The catalyst can keep good catalytic activity in the solution with high methanol concentration. Therefore the Pd/CuO catalyst can be accelerated by increasing the methanol concentration, more adsorption exists between the methanol molecules and hydroxyl on the surface of the catalyst. The adsorption of the methanol molecules can be accelerated by increasing the methanol concentration, more methanol molecules adsorb on the surface of Pd active sites and are oxidized into CO₂, therefore the peak current densities increase. The intermediates adsorbed on the Pd active sites could be oxidized by the CuO due to the bifunctional mechanism. Especially in 4 M methanol solution, the current densities of the catalysts prepared by Ti₃₀Cu₆₅Pd₅, Ti₃₀Cu₆₀Pd₁₀ and Ti₃₀Cu₅₀Pd₂₀, respectively. The curve 4, 5 and 6 in the Bode plots are phase angle-frequency of the catalysts prepared by Ti₃₀Cu₆₅Pd₅, Ti₃₀Cu₆₀Pd₁₀ and Ti₃₀Cu₅₀Pd₂₀, respectively. A.C. impedance spectrum was used to investigate more electro-chemical behavior of the electrocatalysts. Fig. 8 shows the Bode (a) and Nyquist (b) plots in 1 M CH₃OH and 0.5 M NaOH at −0.2 V and the amplitude was 10 mV. The frequencies ranged from 10000 Hz to 0.1 Hz. The curve 1, 2 and 3 in the Bode plots are the |Z| frequency curves of the catalysts prepared by Ti₃₀Cu₆₅Pd₅, Ti₃₀Cu₆₀Pd₁₀ and Ti₃₀Cu₅₀Pd₂₀, respectively. The curve 4, 5 and 6 in the Bode plots are phase angle-frequency of the catalysts prepared by Ti₃₀Cu₆₅Pd₅, Ti₃₀Cu₆₀Pd₁₀ and Ti₃₀Cu₅₀Pd₂₀, respectively. The catalyst prepared by Ti₃₀Cu₆₀Pd₁₀ ribbon showed the best catalytic activity due to appropriate Pd: CuO ratio. Furthermore, the effects of methanol concentration on methanol electro-oxidation reaction were examined. Sample prepared by the Ti₃₀Cu₆₀Pd₁₀ ribbon exhibited the highest reaction order which indicates that the highest catalytic activity in the kinetic aspect. EIS was used to measure the charge transfer resistance of the as-prepared catalysts. The charge transfer resistance increases with the decrease of CuO relative amount in the catalysts, this phenomenon confirms the bifunctional effect of CuO.

Conclusions

In this work, nanoporous Pd/CuO catalysts have been fabricated by a chemical dealloying method. The CV and CA tests show the as-prepared catalysts exhibited excellent electrocatalytic activities which could be due to the bifunctional mechanism. In addition, the catalytic activity of these Pd/CuO nano structure for methanol electro-oxidation depended on the Pd/CuO ratio which could be controlled by the content of the original Ti-Cu-Pd amorphous alloy. It was found that the catalytic activity was improved firstly and then depressed by increasing Pd content within both EASA and methanol electro-oxidation region. The catalyst prepared by Ti₃₀Cu₆₀Pd₁₀ ribbon showed the best catalytic activity due to appropriate Pd: CuO ratio. Furthermore, the effects of methanol concentration on methanol electro-oxidation reaction were examined. Sample prepared by the Ti₃₀Cu₆₀Pd₁₀ ribbon exhibited the highest reaction order which indicates that the highest catalytic activity in the kinetic aspect. EIS was used to measure the charge transfer resistance of the as-prepared catalysts. The charge transfer resistance increases with the decrease of CuO relative amount in the catalysts, this phenomenon confirms the bifunctional effect of CuO.

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