

## Fabrication of Poly(*o*-Methoxyaniline)/Pt-M Nanocomposites and Their Electrocatalytic Activities for Methanol Oxidation

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Poly(*o*-methoxyaniline)/Pt-M (POMA/Pt-M, M=Ru, Au, Pd) composite catalysts have been successfully fabricated by a two-step electrodeposition and used for the methanol electrooxidation. As-prepared composite catalysts are characterized by SEM and electrochemical analysis. The results of the catalytic activity for the methanol electrooxidation show that the composite catalysts have higher catalytic activity and stronger poisoning-tolerance than Pt/GC. And the catalytic activities sequences for the methanol electrooxidation on the different catalysts are Pt-Ru/POMA/GC > Pt/POMA/GC > Pt-Au/POMA/GC > Pt/GC.

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**Keywords:** Conducting polymer, Poly(*o*-methoxyaniline), Platinum nanoparticles, Composite catalyst, electrocatalytic oxidation.

### 1. INTRODUCTION

The direct methanol fuel cell (DMFC) has attracted great attention because of its high-energy conversion efficiency, low operating temperature, low pollutant emission and the simplicity of handling liquid fuel [1,2]. Pt has been extensively used as the catalyst for methanol electrooxidation [3-6]. However, some intermediate products (e.g., CO<sub>ads</sub>) of methanol oxidation reaction are readily and strongly adsorbed on the surface of Pt catalyst, which leads to severe limitations in the oxidation kinetics [7]. In order to improve the catalytic performance of Pt catalyst, an ideal approach is to use multicomponent catalysts [8-10]. In addition, a high dispersed nano-catalyst possesses excellent

electrocatalytic activity [11]. Therefore, it is necessary to develop a good catalyst support for the development of DMFC.

Conducting polymers (CPs) have received an increasing attention due to their potential application in catalysis, sensors, microelectronics technique and anticorrosion coatings [12]. It is well known that electrodeposition is one of the effective methods for the preparation of CPs and its composite materials [5,6,13-17]. CPs with stable three-dimensional structure and are not only electron conducting, but also proton conducting materials which can be proposed as the suitable catalyst supports [18-25]. Up to now, the studies of CPs as host material of Pt nanoparticles are centered on the polyaniline [23,26], polypyrrole [19], polythiophene and their derivatives [27,28]. Among the above CPs, polyaniline and its derivatives are widely used as the host material of catalysts in the electrocatalysis. As one of polyaniline derivatives, poly(*o*-methoxyaniline) (POMA) with good solubility [29,30], electrocatalytic activity [31,32] and thermal stability [33,34] has been widely applied to battery [35], transistor [36] and nanobiotechnology [37,38]. Moreover, monometallic Pt nanoparticles dispersed on POMA films exhibited an enhanced performance for the methanol electrooxidation [39,40]. However, there have been no reports on the bimetallic Pt-M catalysts supported on POMA films.

In this paper, a three-dimensional porous POMA film has been prepared by a simple potentiostatic electrodeposition method in 0.1 M *o*-methoxyaniline + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Pt and its alloy Pt-M (M = Ru, Au, Pd) have also been successfully electrodeposited on the porous POMA films. As-prepared composite catalysts were characterized by SEM and electrochemical methods. The catalytic activities of composite catalysts for methanol electrooxidation were also evaluated by cyclic voltammetry and chronoamperometry.

## 2. EXPERIMENTAL

### 2.1 Materials and instruments

*o*-Methoxyaniline (99%), H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>OH, H<sub>2</sub>PtCl<sub>6</sub>, RuCl<sub>3</sub>, PdCl<sub>2</sub> and HAuCl<sub>4</sub> were analytical-grade purity. *o*-Methoxyaniline was distilled before use. Doubly distilled water was used throughout. The electrochemical experiments were carried out using a CHI 660B potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd., China) at room temperature. Glassy carbon electrode (GC, 3mm diameter) was used as the substrate electrode. The counter electrode and the reference used were platinum wire (0.5mm diameter) and saturated calomel electrode (SCE), respectively. The solutions were deaerated by a dry nitrogen stream and maintained with a slight overpressure of nitrogen during the experiments. A scanning electron microscope (SEM, FEI Quanta 200) was used to determine the morphology of composites.

### 2.2 Preparation of POMA and composite catalysts

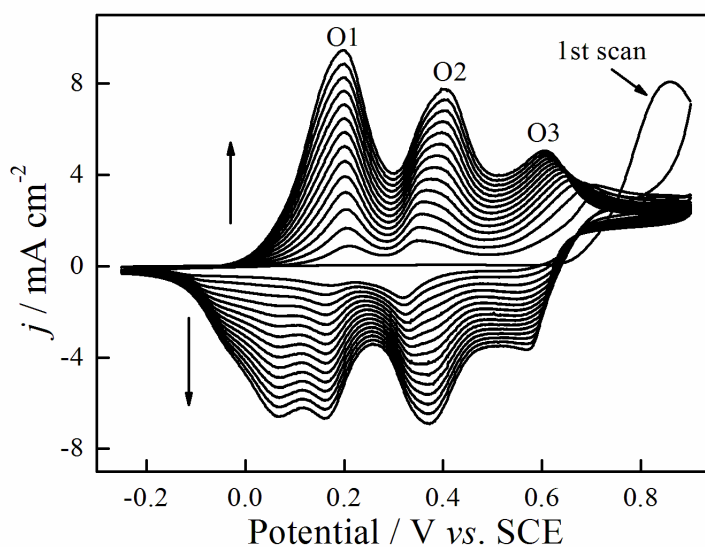
Before modification, GC surface was polished with 0.3 μm alumina slurry, and then rinsed with doubly distilled water in ultrasonic bath. Pt/POMA/GC and Pt-M (M = Ru, Au, Pd)/POMA/GC were

prepared using the following route. Briefly, the electrodeposition of POMA on GC was performed in 0.5 M  $\text{H}_2\text{SO}_4$  solution containing 0.1 M *o*-methoxyaniline at the constant potentials of 0.7 V. And then the POMA-modified GC electrode (POMA/GC) was thoroughly rinsed with ethanol and water. Monometallic Pt nanoparticles were electrodeposited on POMA/GC in a 2.6 mM  $\text{H}_2\text{PtCl}_6$  + 0.5 M  $\text{H}_2\text{SO}_4$  solution at -0.2 V. Bimetallic Pt-M nanoparticles were electrodeposited on POMA/GC, respectively, from 2.6 mM  $\text{H}_2\text{PtCl}_6$  + 2.6 mM  $\text{RuCl}_3$  + 0.5 M  $\text{H}_2\text{SO}_4$  solution (for Pt-Ru/POMA/GC), 2.6 mM  $\text{H}_2\text{PtCl}_6$  + 2.6 mM  $\text{HAuCl}_4$  + 0.5 M  $\text{H}_2\text{SO}_4$  solution (for Pt-Au/POMA/GC) and 2.6 mM  $\text{H}_2\text{PtCl}_6$  + 2.6 mM  $\text{PdCl}_2$  + 0.5 M  $\text{H}_2\text{SO}_4$  solution and (for Pt-Pd/POMA/GC). The amount of metal deposited is determined by controlling the amount of the charge integrated during metal deposition [41].

### 3. RESULTS AND DISCUSSION

#### 3.1 Electrochemical synthesis of POMA

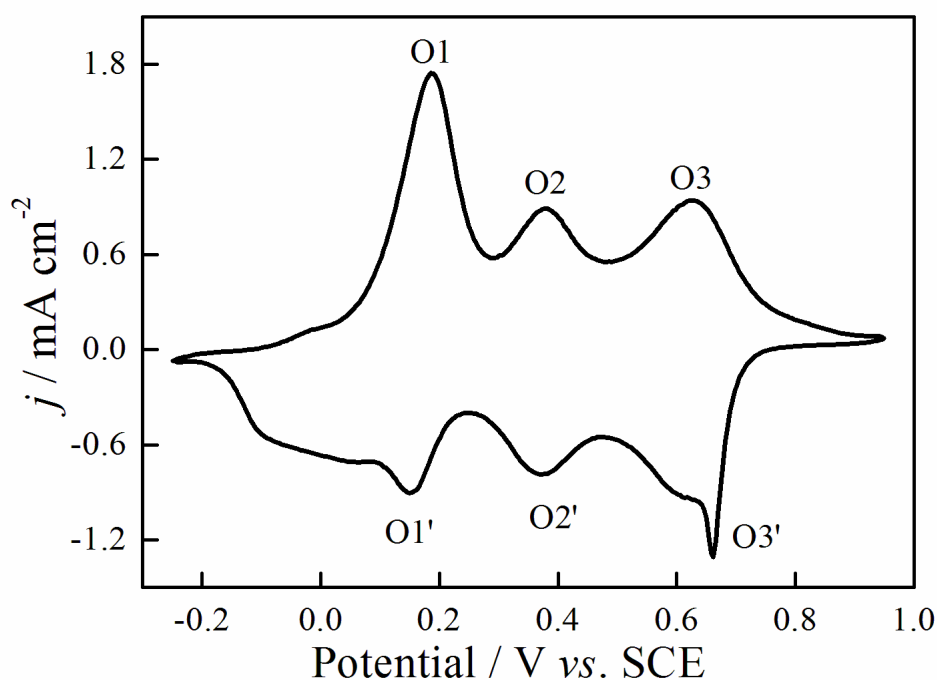
Fig. 1 shows the successive cyclic voltammograms (CVs) of 0.1 M *o*-methoxyaniline on GC in a 0.5 M  $\text{H}_2\text{SO}_4$  solution. As the CV scans continued, a polymer film was formed on the GC surface. The increase of the redox wave currents implied that the amount of the polymer on GC electrode was increasing [42]. In the first positive sweep, the monomer oxidation started at about 0.64 V, and then part of product yielded from *o*-methoxyaniline oxidation was deposited on the electrode, i.e., the polymer growth process was beginning to take place. And the reduction peaks of the polymer appeared during the negative scan. Similar to polyaniline [43,44], the first peak (O1) was related to the oxidation of POMA in the leucoemeraldine oxidation state to the emeraldine oxidation state. The second peak (O2) corresponded to the oxidation of head-to-tail dimer. The third peak (O3) corresponded to the conversion from emeraldine to pernigraniline structure.



**Figure 1.** CVs of 0.1 M *o*-methoxyaniline on GC electrode in 0.5 M  $\text{H}_2\text{SO}_4$  at 50  $\text{mV s}^{-1}$ .

### 3.2 Electrochemical behavior of POMA

In order to get insight into the electrochemical properties of POMA, the CV of POMA was tested in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (Fig. 2). As seen from Fig. 2, POMA had three pairs of cathodic and anodic peaks. It is well known that the smaller difference of ( $E_a - E_c$ ) ( $E_a$  and  $E_c$  are the oxidation and reduction peak potential, respectively) related to the kinetics of the doping-dedoping reactions implies that the redox behavior of polymer is more reversible. In Fig. 2, the difference of ( $E_a - E_c$ ) of the three pairs of the redox peaks were 0.04 V ( $E_{O1} - E_{O1'}$ ), 0.01 V ( $E_{O2} - E_{O2'}$ ) and 0.03 V ( $E_{O3} - E_{O3'}$ ), respectively. Therefore, it was concluded that POMA film had an excellent redox reversibility in H<sub>2</sub>SO<sub>4</sub> solution.



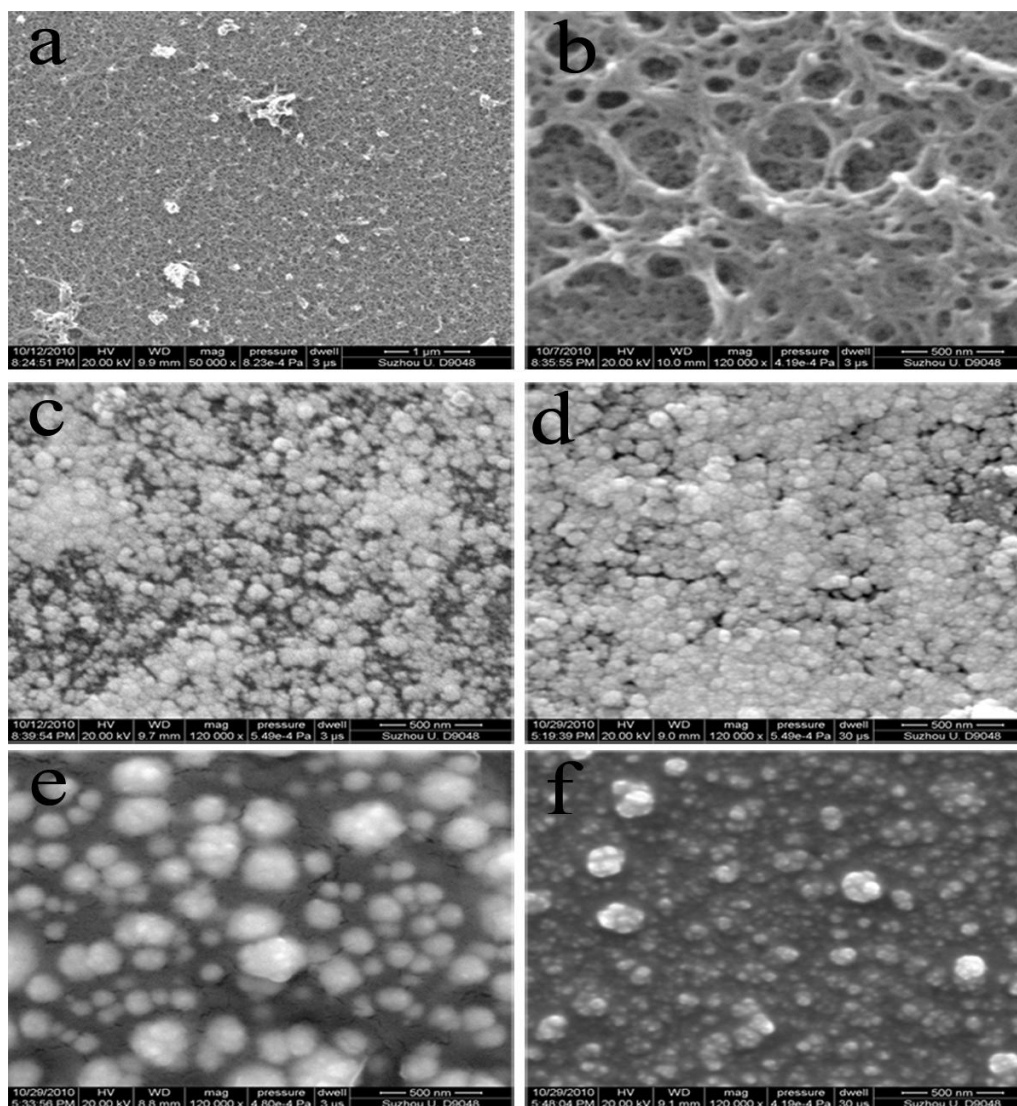
**Figure 2.** CVs of POMA/GC in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 50 mV s<sup>-1</sup>.

### 3.3 Morphologies of POMA and composite catalysts

Fig. 3 shows the SEM images of POMA and different composite catalysts. As seen from Fig. 3a, macroscopically, POMA seems to be smooth and homogeneous. However, microscopically, POMA is a three-dimensional porous network structure (Fig. 3b).

Since POMA acted as a 3D-random matrix, it could provide an environment to disperse the individual Pt or Pt-M nanoparticles.

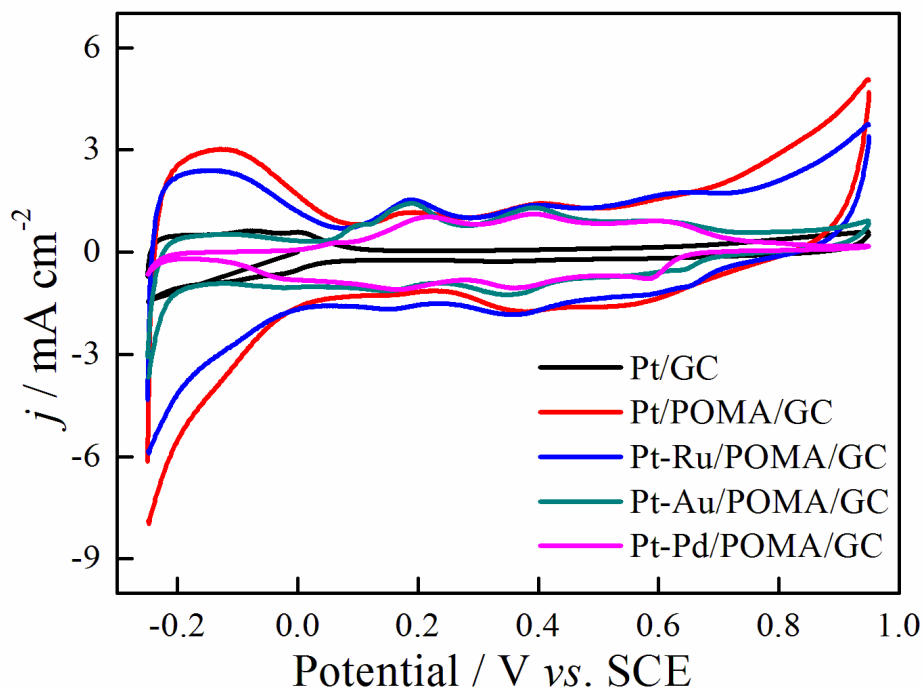
It was seen from Fig. 3c-f, metal nanoparticles were dispersed uniformly on the POMA surface and the morphologies of metal nanoparticles were similar.



**Figure 3.** SEM images of POMA/GC (at low magnification (a) and enlarged magnification (b)), Pt/POMA/GC (c), Pt-Ru/POMA/GC (d), Pt-Au/POMA/GC (e) and Pt-Pd/POMA/GC (f).

### 3.4 Hydrogen adsorption characteristics of composite catalysts

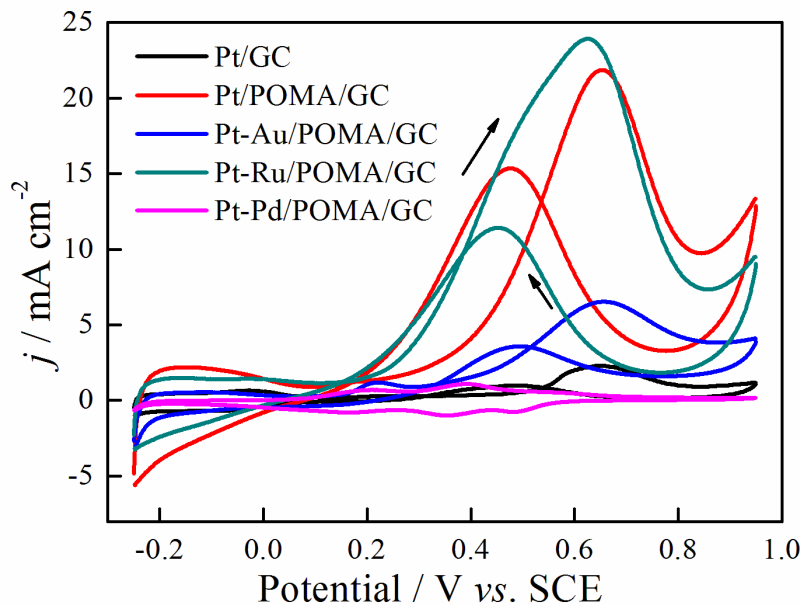
In further electrochemical experiments, CVs of Pt/GC, Pt/POMA/GC, Pt-Ru/POMA/GC, Pt-Pd/POMA/GC and Pt-Au/POMA/GC were tested in 0.5 M H<sub>2</sub>SO<sub>4</sub> (Fig. 4). Except the Pt-Pd/POMA/GC electrode, the characteristic peaks for the hydrogen adsorption/desorption on Pt/GC, Pt/POMA/GC, Pt-Ru/POMA/GC and Pt-Au/POMA/GC electrodes were clearly observed between -0.25 and 0.05 V. Generally, the integrated intensity of hydrogen desorption represented the number of available sites of Pt [45]. As seen from Fig. 4, the integrated areas of hydrogen desorption on the different electrodes decreased in the order of Pt/POMA/GC, Pt-Ru/POMA/GC, Pt-Au/POMA/GC and Pt/GC. From the above results, the integrated intensity of hydrogen desorption on Pt-M/POMA/GC was smaller than that on Pt/POMA/GC. This was due to the presence of M metal in the composite catalysts.



**Figure 4.** CVs of Pt/GC, Pt/POMA/GC, Pt-Ru/POMA/GC, Pt-Pd/POMA/GC and Pt-Au/POMA/GC in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 50 mV s<sup>-1</sup>.

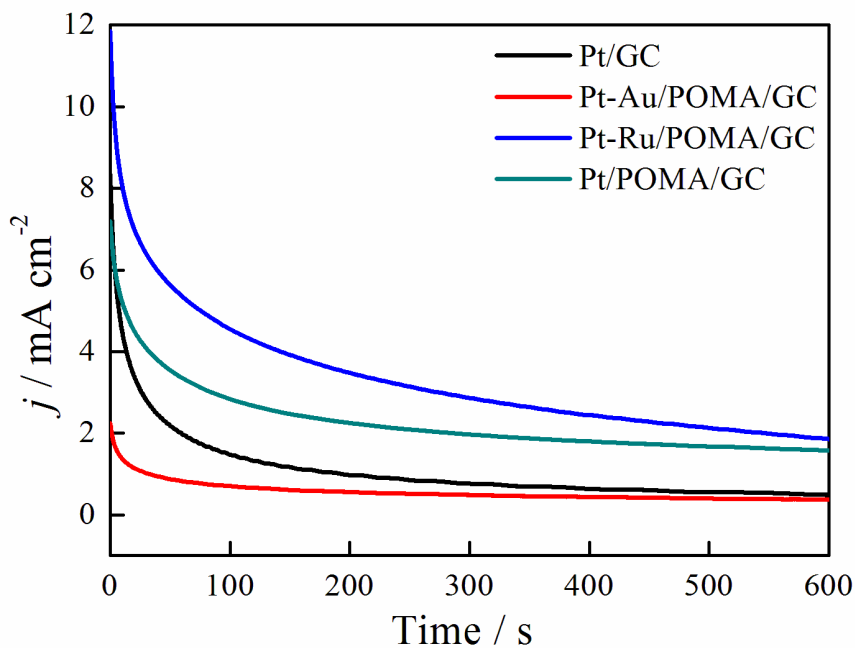
### 3.5 Electrooxidation of methanol

Fig. 5 shows the CVs of methanol oxidation on Pt/GC, Pt/POMA/GC, Pt-Ru/POMA/GC, Pt-Pd/POMA/GC and Pt-Au/POMA/GC electrodes in 1.0 M methanol + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. As observed from Fig. 5, the peak potential of methanol oxidation was around 0.65 V in the anodic sweep of curve. The current density on Pt/POMA/GC was enhanced obviously compared with Pt/GC, which showed that POMA could promote the electrooxidation of methanol. On the other hand, the activity of methanol electrooxidation on Pt-M alloys supported on POMA was also enhanced. For example, the peak current density of methanol oxidation on Pt-Ru/POMA/GC was 9.7, 1.1 and 3.6 times of that on Pt/GC, Pt/POMA/GC and Pt-Au/POMA/GC, respectively. The peak current density of methanol oxidation on Pt-Ru/POMA/GC was almost the same as that on Pt/POMA/GC, however, at a lower potential, the current density of methanol oxidation on Pt-Ru/POMA/GC was higher than that on Pt/POMA/GC. At low potential (for example, at 0.4 V), the oxidation current of methanol on Pt-Ru/POMA/GC was 2.6 times of that on Pt/POMA/GC. On the other hand, the onset oxidation potential on Pt-Ru/POMA/GC was shifted negatively compared with other electrodes. Moreover, we noted that Pt-Pd/POMA/GC did not show any electrocatalytic activity for methanol oxidation. Based on above results, it was concluded that the capabilities of methanol electrooxidation on these electrodes followed the order: Pt-Ru/POMA/GC > Pt/POMA/GC > Pt-Au/POMA/GC > Pt/GC > Pt-Pd/POMA/GC.



**Figure 5.** CVs of methanol oxidation on Pt/GC, Pt/POMA/GC, Pt-Ru/POMA/GC, Pt-Pd/POMA/GC and Pt-Au/POMA/GC electrodes in 1.0 M CH<sub>3</sub>OH and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at potential scan rates of 50 mV s<sup>-1</sup>.

The typical chronoamperometric curves on Pt/GC, Pt/POMA/GC, Pt-Ru/POMA/GC and Pt-Au/POMA/GC electrodes in 1.0 M methanol + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution were recorded, as shown in Fig. 6.



**Figure 6.** Chronoamperometric curves (at 0.6 V) of methanol oxidation on Pt/GC, Pt/POMA/GC, Pt-Ru/POMA/GC and Pt-Au/POMA/GC electrodes.

When the applied potential was 0.6 V, the decay trend of current density of methanol oxidation on the four electrodes was different. Due to the continuous oxidation of methanol on the catalyst surface, tenacious reaction intermediates such as  $\text{CO}_{\text{ads}}$  would begin to accumulate if the kinetics of the removal reaction could not keep pace with that of methanol oxidation. A slow decay of oxidation current density with time implies that the catalyst has good poisoning-tolerance ability [23,46]. As seen from Fig. 6, the decay of current density for methanol oxidation on Pt-Ru/POMA/GC was significantly slow. And at the end of the test, the oxidation current on Pt-Ru/POMA/GC retained largest among these electrodes. This indicated that Pt-Ru/POMA/GC had the best poisoning-tolerance performance for methanol oxidation.

#### 4. CONCLUSIONS

In this paper, POMA/Pt-M (M=Ru, Au, Pd) composite catalysts were successfully fabricated by the electrochemical method and their electrocatalytic performances for the methanol electrooxidation in  $\text{H}_2\text{SO}_4$  solution were investigated. The results showed that POMA and Pt-M bimetal modified GC electrode improved significantly the catalytic activity of Pt nanoparticles for methanol electrooxidation. Additionally, the activity of methanol oxidation on these composite electrodes followed the order: Pt-Ru/POMA/GC > Pt/POMA/GC > Pt-Au/POMA/GC > Pt/GC.

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