

Electrochemical Modification of Pt/C Catalyst by Silicomolybdic Acid

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Abstract: Modification of conventional Pt/C electrocatalyst with silicomolybdic acid (SiMoA) was performed using electrochemical cyclic voltammetry method. The modified and unmodified catalysts were tested under identical conditions for electrooxidation of CO, methanol, and ethanol. In the CO-stripping experiments, the modified catalyst was characterized by significant shifts (80 and 60 mV) to lower onset potential and peak potential for CO electrooxidation, suggesting better CO-tolerant property of the modified catalyst. In the electrooxidation of methanol and ethanol, the modified catalyst was featured by significantly increased current densities due to reduced residence time of the reaction intermediates, showing significantly higher electrocatalytic activity for the electrooxidation of alcohols.

Key Words: PEMFCs (proton exchange membrane full cells); CO tolerance catalyst; Silicomolybdic acid; CO electrooxidation; Alcohol electrooxidation

Proton exchange membrane fuel cells (PEMFCs) have been considered as highly efficient power transfer assemblies with low noises and near zero-emission. At present, platinum seems to be indispensable for the electrocatalyst in PEMFC technology. Much attention has been devoted to the development of efficient anode electrocatalysts having high CO tolerant/removal property and/or high activity and stability for the electrooxidation of lower alcohols and other small organic molecules. The use of redox transition metal oxides, such as RuO₂, MoO₃, and WO₃, as promoter or cocatalyst of Pt/C in the electrode can significantly lower the oxidation potential of CO and methanol, and therefore improve the CO tolerant property of the Pt-base electrode catalyst^[1–3].

Silicomolybdic acid (SiMoA) and its salts are inorganic macromolecules with flexible acidic and redox properties that find many applications in heterogeneous catalysis, e.g., in catalytic dehydrogenation of alcohols^[4–5]. Because of their good ionic conductivity and thermal stability, heteropolyacids have also been used as additives in polymer-based electrolyte to enhance the ionic conductivity, thermal and electrochemical stability of the polymer electrolytes. In the work of Arico *et*

al.^[6], solution of phosphotungstic acid (PWA, i.e., H₃PW₁₂O₄₀) itself was used as an electrolyte to promote the electrooxidation of CO, CO/H₂, and methanol; the results showed that the PWA electrolyte promote the methanol electrooxidation by increasing the rate of water discharge at the electrode. We are wondering why the redox and ionic conductive properties of SiMoA could make the material an efficient oxidant displaying fast reversible multi-electron redox transformations under mild condition, which could find further application as efficient promoter or cocatalyst for the Pt-based electrocatalyst in PEMFCs technology using methanol or other small organic molecules as fuel. In this article, the conventional Pt/C electrode was electrochemically modified with SiMoA. Electrochemical oxidation of CO, CH₃OH, and C₂H₅OH were studied, over the modified and unmodified electrodes to understand the promoter function of SiMoA on the electrocatalytic performance of the Pt/C catalyst.

1 Experimental

1.1 Electrochemical modification of Pt/C catalyst by silicomolybdic acid

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The electrochemical modification of Pt/C catalyst was conducted in a mixture electrolyte solution of $0.25 \text{ g}\cdot\text{L}^{-1}$ SiMoA ($\text{H}_4\text{SiMo}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$) and $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 . Pt/C catalyst was obtained by Pt deposition onto the well-known Vulcan XC-72 carbon using a modified colloid method, as described in literature^[7]. The Pt loading in the catalyst is 20% (w).

The catalytic electrodes were prepared by the conventional ink method. The catalyst inks were prepared by mixing 5 mg catalyst with 0.25 mL isopropanol, followed by the addition of 20 μL 5% Nafion-isopropanol solution and then ultrasonic dispersion for 15 min. Fifty microlitres of the ink was pasted onto a carbon paper (Toray, TGP-H-090) to prepare the working electrode with a Pt loading of ca. $0.2 \text{ mg}\cdot\text{cm}^{-2}$. A three-electrode cell, with a saturated calomel electrode (SCE) as the reference electrode and a Pt foil (1 cm^2) as the counter electrode, was used for the electrochemical modification by cyclic voltammogram at 298 K in the mixture electrolyte for up to 10 cycles from -0.2 to 1.0 V at a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$. The electrochemical potential data in this work were calibrated to the SCE value. The electrochemical modification and electrochemical measurements were performed on a CHI-630A (Chenhua Instrument Co., Shanghai) electrochemical system.

1.2 Electrooxidation of CO, methanol, and ethanol

The electrochemical measurements were carried out in a three-electrode cell at 298 K. Unless specified, the electrolyte solutions were first deaerated with high-purity (HP, 99.999%) nitrogen prior to any measurement. For the CO-stripping measurement, pre-adsorption of CO on the electrode catalyst was carried out by bubbling carbon monoxide (UHP grade) through the electrolyte for 10 min, followed by purging with HP nitrogen for 20 min to remove any residual CO in the solution. The CO stripping CV curve was obtained from two consecutive scan cycles between -0.2 and 1.0 V with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ in $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 solution.

Both chronoamperometry and cyclic voltammetry methods were used to study the electrooxidation of methanol and ethanol over both the modified and unmodified electrodes. The electrolyte was $0.5 \text{ mol}\cdot\text{L}^{-1}$ $\text{CH}_3\text{OH}+0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 or $0.5 \text{ mol}\cdot\text{L}^{-1}$ $\text{C}_2\text{H}_5\text{OH}+0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 . The scan rate was $20 \text{ mV}\cdot\text{s}^{-1}$ in CV and the potential was fixed at 0.65 V in the chronoamperometry measurement.

2 Results and discussion

2.1 Electrochemical modification of Pt/C by SiMoA

Fig.1 shows the modification process of the Pt/C catalyst by electrochemical deposition of SiMoA in consecutive 10 scan cycles of the cyclic voltammetry measurements. After the first scan cycle, two pairs of reversible redox peaks were observed on the CV curves at 0.19 and 0.29 V . These peaks can be assigned to the oxidation and reduction of two different oxida-

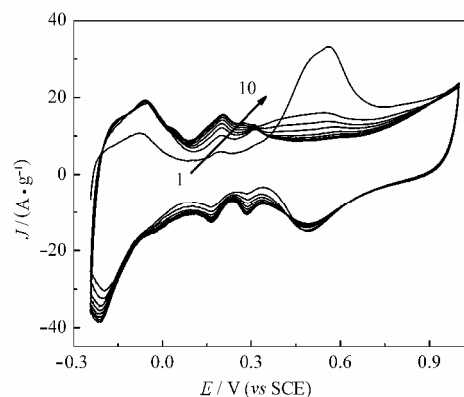


Fig.1 Cyclic voltammograms of SiMoA modification on Pt/C electrocatalyst at 298 K

electrolyte solution: $0.25 \text{ g}\cdot\text{L}^{-1}$ SiMoA+ $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 ; scan rate: $20 \text{ mV}\cdot\text{s}^{-1}$; 298 K; 1–10 cycles; J : current per mass of Pt

tion states of molybdenum in the species associated with the depositing SiMoA molecules. The increment in peak current of each scan cycle decreased with increasing the number of scan cycles. Also, the peak currents on the CV curves became constant when the system was consecutively scanned for more than 10 cycles, indicating that there is a “saturation” amount for the deposition of SiMoA at the anode surface during the electrochemical modification process.

Fig.2 shows the cyclic voltammograms of the modified and unmodified Pt/C catalysts in $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 . As shown in Fig.1, the redox peaks around 0.19 V on the modified Pt/C catalyst strongly supports the deposition of SiMoA at the electrode catalyst during the electrochemical modification process. The CV curve showed no obvious change when the modified electrode was consecutively scanned for more than 10 cycles, indicating that the interaction of SiMoA with the electrode surface is sufficiently stable. These observation also suggest that the redox reaction associated with signals around 0.19 V is completely reversible, probably due to the use of a slow sweep rate ($10 \text{ mV}\cdot\text{s}^{-1}$). Thus, the number of electrons (n)

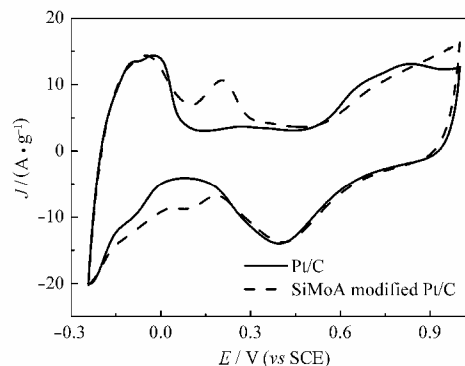


Fig.2 Cyclic voltammograms of the Pt/C catalysts modified and unmodified by SiMoA

in $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 at 298 K with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$

involved in the redox reaction can be calculated from the difference in peak potentials (ΔE_p in mV) associated with the oxidation and reduction reaction using the equation^[8]:

$$n=60/\Delta E_p$$

In Fig.2, ΔE_p equals 35 mV and the number of electrons (n) involved in the reaction is about 2. Therefore, the signals on the CV curve of the modified electrode catalyst can be attributed to a redox process between Mo^{4+} and Mo^{6+} .

Both the modified and the unmodified Pt/C catalysts showed clear hydrogen adsorption/desorption capability featured by two hydrogen-desorption and two hydrogen-adsorption peaks on the low-potential side of their CV curves in Fig.2, which are in contrast with the behavior of polycrystalline Pt electrocatalyst that gave two hydrogen-adsorption but three hydrogen-desorption peaks^[9]. In comparison with the unmodified catalyst, the modification with SiMoA resulted in an overall shrinkage of the hydrogen adsorption/desorption peaks in Fig.2, implying a decrease in the number of active Pt sites after the modification.

2.2 CO stripping on Pt/C modified by SiMoA

Fig.3 shows the CO-stripping cyclic voltammograms of the unmodified and SiMoA modified Pt/C catalysts. Modification of Pt/C catalysts by SiMoA resulted in negative shifts for the onset potential and peak potential of CO electrooxidation by 80 and 60 mV, respectively. The lower onset potential and peak potential of CO oxidation mean an easier removal of the pre-adsorbed CO, thus suggesting an improved CO tolerant property as a result of SiMoA modification.

Furthermore, the charge for CO oxidation (Q , $\text{mC}\cdot\text{cm}^{-2}$), obtained from the integral area of CO-stripping peak in the CV curves, can be used to calculate the electrochemical active surface area (EAS, $\text{m}^2\cdot\text{g}^{-1}$) of Pt according to the following equation^[10]:

$$\text{EAS} = \frac{Q}{0.420m}$$

where m is the Pt loading on the electrode, and the value in the denominator, 0.420 ($\text{mC}\cdot\text{cm}^{-2}$), refers to the charge required for the removal of CO monolayer on polycrystalline Pt, assuming a linear adsorption of CO on Pt surface. The EAS of unmodified Pt/C is $58.3 \text{ m}^2\cdot\text{g}^{-1}$, while that for the modified one is somewhat lower ($42.6 \text{ m}^2\cdot\text{g}^{-1}$). The smaller EAS for the modified catalyst means that less Pt atoms are involved in the electrochemical oxidation of CO, suggesting that the utilization of Pt atoms is decreased after modification by SiMoA. Similar results have also been reported by Jusys *et al.*^[11] on ternary Pt-based catalyst after modification by metal oxides. Since the adsorption of CO is more likely on the noble metal surface sites, the present observation could be attributed to the partial coverage of Pt surface by SiMoA molecules. Fig.3 also shows that the double-layer capacitance of modified Pt/C is higher than that of the unmodified one, which might be due to

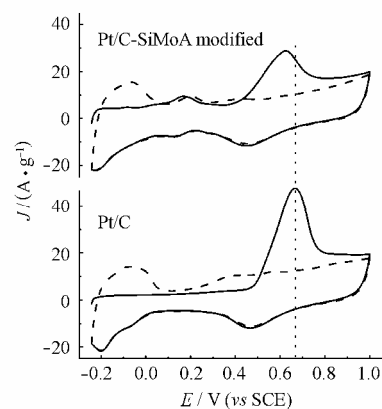


Fig.3 CO-stripping cyclic voltammograms of the Pt/C catalysts modified and unmodified by SiMoA in $0.5 \text{ mol}\cdot\text{L}^{-1} \text{H}_2\text{SO}_4$ at 298 K with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$, solid lines are CO-stripping CV curves, while dashed lines are CV curves in the absence of any CO

the strengthened hydrophilicity of the catalyst surface by the adsorption of polar SiMoA molecules.

2.3 Effect of the SiMoA modification in methanol electro-oxidation

The cyclic voltammograms of methanol electrooxidation on modified and unmodified Pt/C catalysts are shown in Fig.4(a). The onset potential of methanol electrooxidation on the unmodified Pt/C was 0.13 V. A significant shift from 0.13 to 0.11 V can be observed after the SiMoA modification. Although the peak potentials for methanol electrooxidation were only more or less affected, the corresponding peak current increased significantly from $105 \text{ A}\cdot\text{g}^{-1}$ (unmodified Pt/C) to $125 \text{ A}\cdot\text{g}^{-1}$ (modified Pt/C). Chronoamperometry measurement at 0.65 V was further performed to evaluate the effect of SiMoA modification on the catalyst stability (Fig.4(b)). A higher current density was observed on the modified catalyst, which is in agreement with the results of CV measurement (Fig.4(a)). However, both modified and unmodified catalysts showed similar behavior in chronoamperometry measurements, suggesting that the catalyst stability in methanol electrooxidation is not affected by the SiMoA adsorption.

2.4 Effect of the SiMoA modification in ethanol electro-oxidation

The cyclic voltammograms of ethanol electrooxidation on the unmodified and SiMoA modified Pt/C are shown in Fig.5(a). A more significant increase in peak current from 118 to $143 \text{ A}\cdot\text{g}^{-1}$ was observed as a result of SiMoA modification. Contrary to the observation in methanol electrooxidation, the onset potential for ethanol oxidation was not changed by SiMoA modification. A new peak at about 0.40 V, which might be due to ethanol oxidation to acetaldehyde^[12], was also detected. Furthermore, chronoamperometry measurement at

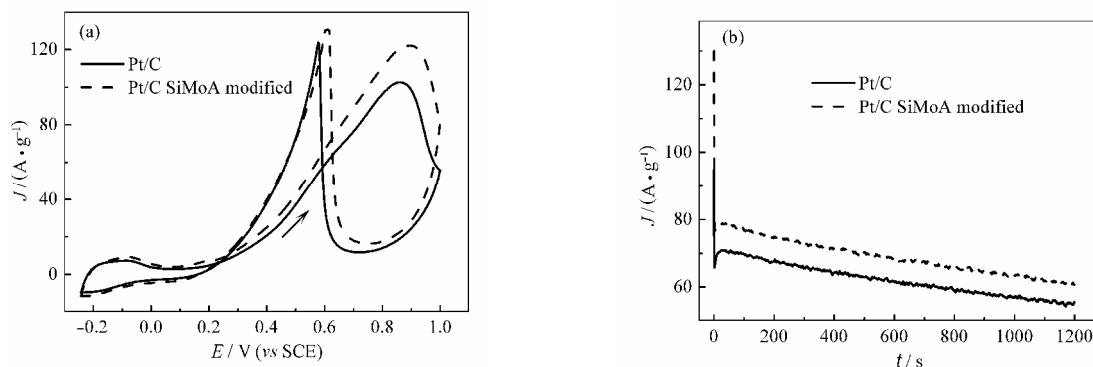


Fig.4 Methanol electrooxidation curves of Pt/C catalysts modified and unmodified by SiMoA in $0.5 \text{ mol}\cdot\text{L}^{-1} \text{CH}_3\text{OH} + 0.5 \text{ mol}\cdot\text{L}^{-1} \text{H}_2\text{SO}_4$ at 298 K; (a) CV curves with a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$; (b) current–time curves at 0.65 V

0.65 V revealed that the current density on the SiMoA modified Pt/C was much higher and dropped more slowly than that on the unmodified one, indicating an improvement in the activity and stability of Pt/C catalyst by SiMoA modification.

As the SiMoA adsorption on the electrode surface and the stability of the adsorbed SiMoA has been proved by the repeated CV measurements (Fig.2) as well as by the calculated EAS, the decrease in the onset potential in methanol oxidation, and the significant increases in the corresponding peak current in both methanol and ethanol oxidation as results of SiMoA modification of Pt/C catalyst suggest the enhanced activity of the modified catalyst for the oxidation of these lower alcohols.

The cage-like structure of heteropolyanions in SiMoA would affect the adsorption and/or reaction of some polar molecules on the electrode surface^[13]. The increase in the double-layer capacitance of modified Pt/C (Fig.3), possibly due to the strengthened hydrophilicity of the catalyst surface by the adsorption of polar SiMoA molecules, could reinforce the interaction between the catalyst surface and alcohols. Such interaction might favor the activation of alcohols on surface, e.g., the dehydrogenation of alcohols, and such interaction might also be essential to enlarge the reaction field, to accelerate the process of charge transfer among the interface or at the rate-determining step, and finally to promote the electro-

chemical reaction of lower alcohols^[14].

On the other hand, CO-stripping cyclic voltammetry has shown unambiguously that the modification of Pt/C by SiMoA can facilitate the removal of adsorbed CO, an important intermediate reaction during the oxidation of lower alcohols, as manifested by the significant negative shifts of the onset potential and peak potential of CO electrooxidation. Moreover, the promoted desorption of other reaction intermediates during lower alcohol oxidation by the adsorption of Mo atoms at high oxidation state might also be responsible for the improved activity in lower alcohol electrooxidation^[15]. Apparently, the promoted oxidative elimination of reaction intermediate such as CO by SiMoA modification would accelerate the overall reaction.

The negative shift of onset potential in methanol oxidation, and the absence of this effect in ethanol oxidation might be because of the fact that the bigger size of the molecule and higher energy of C–C bond in ethanol inhibit its activation. On the other hand, the increases of oxidation current densities for both the methanol and ethanol oxidation as results of SiMoA adsorption, could be explained by the improved removal of reaction intermediates such as CO. However, detailed kinetic investigation is needed to elucidate these questions.

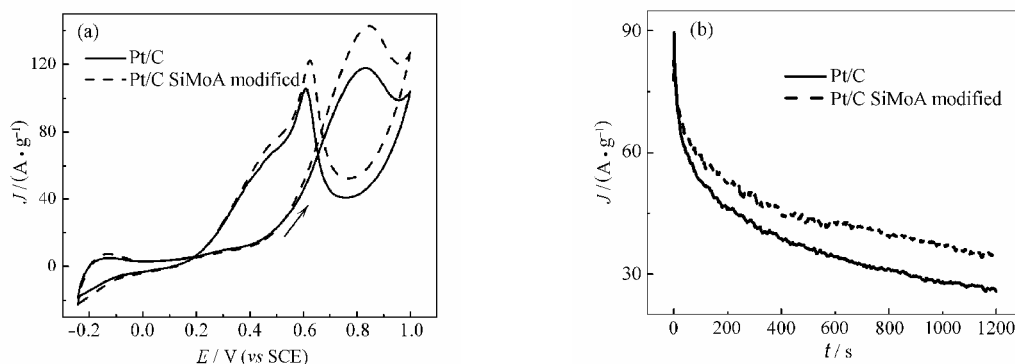


Fig.5 Ethanol electrooxidation curves of Pt/C catalysts modified and unmodified by SiMoA in $0.5 \text{ mol}\cdot\text{L}^{-1} \text{C}_2\text{H}_5\text{OH} + 0.5 \text{ mol}\cdot\text{L}^{-1} \text{H}_2\text{SO}_4$ at 298 K; (a) CV curves with a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$; (b) current–time curves at 0.65 V

3 Conclusions

The conventional Pt/C electrocatalyst was modified with SiMoA by cyclic voltammetry method. The deposited SiMoA molecule was quite stable and showed a redox process between Mo^{4+} and Mo^{6+} during cyclic voltammetry measurement. CO-stripping CV measurements showed that the onset potential and peak potential for CO electrooxidation over SiMoA modified Pt/C are 80 and 60 mV lower than those on the unmodified one, respectively, suggesting an improved CO-tolerant property of the modified catalyst. The cyclic voltammetry and steady-state chronoamperometric measurements revealed that the onset potential in methanol oxidation was lowered, while the corresponding peak currents in both methanol and ethanol oxidation were significantly increased as results of SiMoA modification, suggesting the enhanced activity of the modified catalyst for the oxidation of these lower alcohols. The promotion role of adsorbed SiMoA species are mainly associated with their abilities to facilitate the removal of reaction intermediates, especially the oxidative elimination of CO.

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