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The Spectra Characterization of Mo-S-Ag Cluster Compounds Modified Silver Electrodes and Their Electrochemical Activities

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Abstract: The modified electrodes of Mo-S-Ag cluster compound films on silver surface were investigated by FT-IR, FT-Raman and XPS. The new modified electrodes were applied to the catalytic oxidation of ascorbic acid. This sort of catalytic effects can be inferred because the oxidation peak potentials of ascorbic acid moved to more negation compared with the bare Ag electrode and the oxidation peak currents increased with the increasing of ascorbic acid concentration. The overpotentials of ascorbic acid were significantly reduced. CV measurement revealed the linear relationship between the oxidation peak current and the concentration of ascorbic acid ranging among 0.001 ~ 0.06 mol/L.

Key words: Mo-S-Ag cluster compounds modified electrode; Spectra characterization; Ascorbic acid ; Electrochemical activities

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Mo-S-Ag簇合物膜化学修饰电极的谱学性质及其电化学行为研究

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【摘　要】用FT-IR、FT-Raman和XPS研究Mo-S-Ag化学修饰电极的谱学性质、组成和结构。通过循环伏安法研究这种化学修饰电极对抗坏血酸的催化作用。结果表明，在修饰电极上抗坏血酸的氧化峰电位较裸银电极有明显的变化。研究了抗坏血酸浓度、缓冲溶液酸度、扫描速度及修饰时间等条件变化时，抗坏血酸的氧化峰电位和峰电流的变化。

【关键词】Mo-S-Ag簇合物膜化学修饰电极；谱学性质；抗坏血酸；电化学行为

0 Introduction

Many scientists have great interest in transition metal thiometalates because of their unique characteristics in complex and domains of bioinorganic chemistry, nutrition physiology and many other fields. Numerous Mo(W)-S-Ag cluster compounds containing these thiometalates units with various framework structures have been synthesized and investigated. However, there still some new areas ambiguous for us such as their performance and reactivity on a metal surface[1].

Ascorbic acid is vital in the diet of humans and is present in mammalian brain in the presence of several neurotransmitter amines including

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dopamine, epinephrine and norepinephrinep. As have been manifested, Mo-S-Ag cluster compounds can be formed on a silver surface via interface reaction of MoS_4^{2-} with silver electrode. This new sort of electrodes were long-lived and stable. Thus, this kind of modified electrode can be employed in catalytic oxidation of Ascorbic acid. Compared with bare Ag electrode, the oxidation peak potential moved to more negation. The overpotential decreased greatly. The present investigation aimed at the Mo-S-Ag cluster compounds modified silver electrodes and their catalytic effects on the oxidation of ascorbic acid. The cycle voltammograms (CV) measurement showed a linear relationship between the oxidation peak current and the concentration of ascorbic acid in the range of 0.001 ~ 0.06 mol/L with a correlation coefficient of 0.9936.

1 Experimental

1.1 Apparatus

An IF66V FT-IR spectrometer was adopted to research the reflection and transmission spectra, the sample was for 100 cycles. FT-Raman determination was performed on a RFS100 spectrometer, the sample was scanned for 500 cycles. The XPS spectra were recorded on a Perkin-Elmer PHI550 ESCA SAM electron spectrometer with a Al X-ray anode. The high resolution spectra were measured with the energy analyzer operating in a constant analyzer transmission energy mode at a pass energy of 50 eV. The voltage and current for analysis were 10 kV and 30mA. A 6x6 mm^2 scan area was used for depth profiling studies. The electrochemical experiments were carried out with a M237 electrochemical analyzer (EG&G). A three electrode system was employed with a saturated calomel reference electrode (SCE) and a platinum auxiliary electrode. The working electrode was a 2 mm-diameter silver disk electrode.

1.2 Reagents and chemicals

$(NH_4)_2MoS_4$, $(NH_4)_2MoSO_3$ and $(NH_4)_2MoS_2O_2$ were parpared according to literature[2]. Ascorbic acid (>99.7%) was from Shanghai Biochemistry Research Institute. Silver was from the Shanghai Dian Guang Device works with the purity of 99.99%. All of other reagents were of analytical grade. All solutions were prepared with double distilled water. All solutions tested were deaerated with high purity nitrogen. Experiments were carried out at room temperature.

1.3 Sample preparation

Silver foils (1×1 cm^2, 0.3 mm thick) were polished with abrasive paper and MgO powder consecutively, then dipped into 2 mol/L HNO_3 until small bubble appeared on the surface, the grease and the oxides on silver were thus removed during the whole procedure. Rinsed with deionized water, the silver foils were immersed in 0.002mol/L $(NH_4)_2MoOS_3$ and $(NH_4)_2MoO_2S_2$ solutions respectively for 30 minutes at room temperature, the former showed a thick-gray color while the latter showed as thick-yellow. Then, the plates were rinsed the plate thoroughly with distilled water and acetome respectively, dried by a cold air blast immediately.

1.4 Electrode modification and procedure

Before the experiment, the substrate electrode should be pretreated so as to remove the surface oxides. Firstly, polished the silver electrode by rough and fine sand paper. Then, treated with the same way as the silver foil was prefilmed. Finally, immersed the silver electrode in a 0.00015 mol/L thiomolybdate solution for 2 minute and thoroughly rinsed with double distilled water. The buffer solution was 0.1mol/L NaH_2PO_4 ~ NaOH (PH=7.0). In order to remove the oxygen from the buffer solution, we bubbled the solution with prepurified nitrogen.

2 Results and discussion

2.1 FT-IR and FT-Raman

characterization

The major IR absorption data of the Mo-S-Ag cluster films, thiomolybdates and their cluster ions are showed in Table 1. Table 1 showed that the stretching vibration frequencies of Mo-S-Ag appear at 485 cm^{-1} for free $(NH_4)_2MoOS_3$. The modified silver electrode appeared at 582.9, 562.0, 509.2 and 474.0, 454.8 cm^{-1}. The result indicated that the sulfur atoms should be classified into two kinds in accord with their status in the reaction. One is the bridged sulfur, their Mo-S bonds in Mo-S-Ag bridges are weaker and longer than those in uncoordinated ions. Therefore, their stretching vibrational frequencies reduce to 474.0,454.8 cm^{-1} [3]. The other is terminal sulfur, their Mo-S bonds are shortened and strengthened, causing a blue shift to 582.9, 562.0 and 509.2 cm^{-1}. The information we get from the IR is coincided to the Mo-S vibration in Mo-S cluster compounds[3]

Table 1 Principal IR Absorption Data(cm^{-1}) of the Mo-S-Ag Cluster Films, Thiomolybdates and Their Cluster Ions

Specimen	v_{Mo-S}(term)	v_{Mo-S}(br)	v_{Mo-S}(term)
$(NH_4)_2MoS_4$	480		
$(NH_4)_2MoOS_3$	485	835	
$(NH_4)_2MoO_2S_2$	490		792, 830
the $(NH_4)_2MoS_4$ treated film	592, 508, 490	459, 443, 418, 407	768
the $(NH_4)_2MoOS_3$ treated film	583, 562, 509	474, 454	762, 839
the $(NH_4)_2MoO_2S_2$ treated film	583, 562, 510	483	760, 796, 838
$[Ag(MoOS_3)_2]^{3-}$	500, 492,	458, 446	896, 884

The FT-Raman scattering record gave us further evidence [$(NH_4)_2MoOS_3$]. The peak at 341.6 cm^{-1} must be thecharacteristic signal of Ag-S bond due to the formation of Mo-S-Ag bridges. The peak at 582.7 and 575.1 cm^{-1} probably indicated the terminal Mo-S while the peak at 416.3 cm^{-1} should be the bridged Mo-S. It can be inferred that the modified electrode might be composed of Mo-S-Ag clusters.

As for free $(NH_4)_2MoO_2S_2$, the Mo-S stretching viabration frequencies bonds presented at 490 cm^{-1}. For the modified electrode they appear at 583.0, 562.5 and 483.2 cm^{-1}. The former can be assumed as terminal while the latter was bridged[4].

2.2 XPS characterization

XPS were used to determine the Mo-S-Ag film. It showed the survey X-ray photoelectron spectum [$(NH_4)_2MoOS_3$]. It proved the presence of Mo, O, Ag, S on the surface. The electron spectra of the modified electrode before and after sputtering are carried out. The signal of O was decreased while the Mo, S, Ag were still evident after sputtering for about 7 minute. Hence, we can infer that the modified layer on the electrode surface was composed of Mo, S and Ag. This conclusion was suited with FT-IR and FT-Raman results. It exhibited the peak height vs sputter time which illstruted the film's depth and formation. At the beginning of sputting, O Was 36.02%, Mo was 6.07%, Ag was 35.26% and the S was 22.65%.

XPS of the other modified electrode [$(NH_4)_2MoO_2S_2$] showed us there were Ag, Mo, C, S, O in the surface. After sputting for 3 minutes, peak of Mo, S, Ag were still apparent but the O was decreased. Thus, we gained the same conclusion as above that the modified layers were composed of Mo-S-Ag cluster compounds. Its peak height vs sputter time. This film was thinner than that above.

2.3 Electrochemical behavior of Ascorbic acid at the modified electrode

2.3.1 Ag/$(NH_4)_2MoOS_3$

The cyclic voltammogams (CV) was used to research electrochemical activity of the modified electrode. Fig 1 (a) (c) was the bare Ag electrode and the modified electrode in 0.1mol/L phosphate buffer solutions (PBS) of pH 7.0. Fig 1(b)(d) showed the bare Ag electrode and the modified electrode in 0.2mol/L ascorbic acid. It can be seen that there was no oxidation peak appeared at the bare Ag electrode while a apparent oxidation peak existed at the modified electrode .The peak potential presented at about 0.1 V. Compared with the bare Ag electrode, the overpotential decreased.

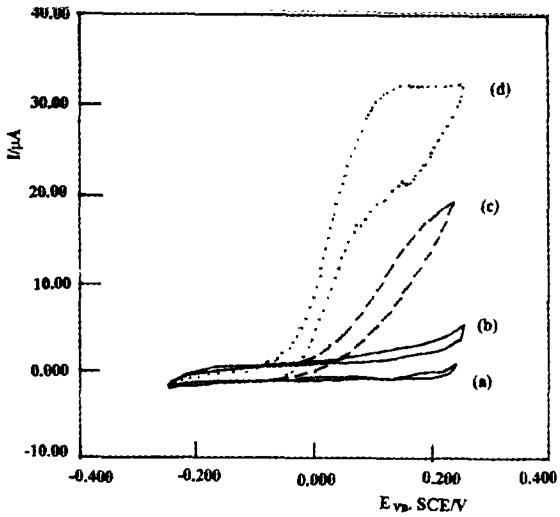

Fig 1 The CV obtained at bare Ag electrode and the modified electrode in 0.1 mol/L PBS of PH 7.0 (a) (b) (c)(d) show the CV obtained for o.ol mol/L ascorbic acid at the bare Ag electrode and Mo-S-Ag modified electrode

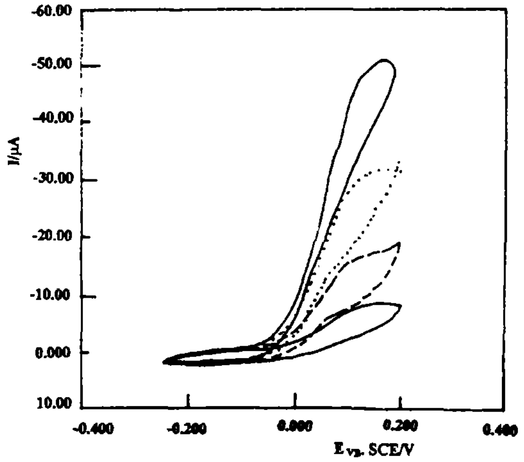

Fig 2 CV of different concentration ascorbic acid at the modified electrode

The cyclic voltammograms at the modified electrode in different concentration of ascorbic acid were showed in Fig 2. We can draw a conclusion that the oxidation wave increased in accordance with the increase of ascorbic acid concentration. Differential pulse voltammetric response (DPV) of the above information were showed in Fig 3. We found a linear relationship between the oxidation peak current and the concentration of ascorbic acid. This relationship was illustrated in Fig 4. This linear relationship existed in the range of 0.001 ~0.06 with the correlation coefficient of 0.9936.

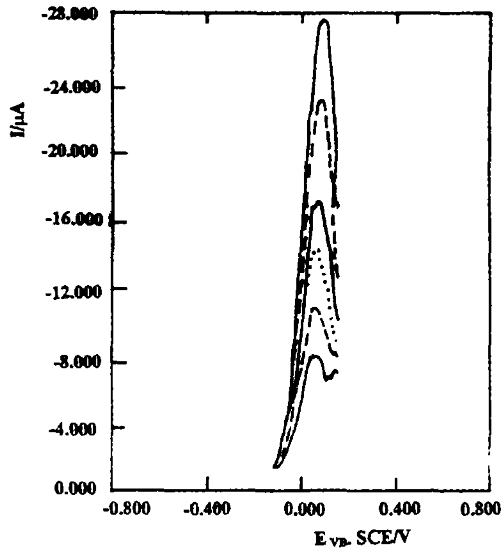

Fig 3 Repersentative DPV curve of different concentration at the modified electrode

According to this linear relationship, we did some experiments to inspect the quantity of ascorbic acid in marketing Vitamin C. The average value of seven determinations was 97% with 0.09 relative standard deviation which is fitted to the chemistry dictionary.

The experimental results showed the anodic peak current increased with the san rate increasing from 20 mV/s to 300 mV/s in PH 7.0 PBS with 0.003 mol/L ascorbic acid, which explain that the reaction is control by diffusion. Which is exhibited in Fig 5.

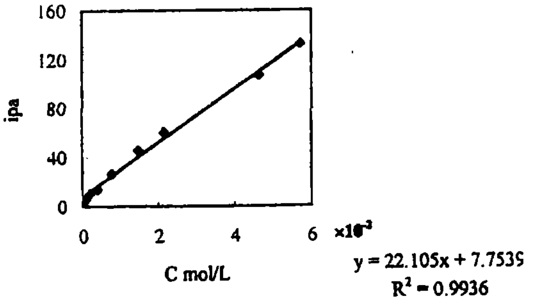

Fig 4 Plots of ip vs concentration of ascorbic acid

The relationship between the catalytic peak at the modified electrode and pH was also been investigated. The experimental results showed that the peak shifted to more negative potentials with increasing of PH gradually in range of PH=5~9.

2.3.2 Ag/$(NH_4)_2MoO_2S_2$

The reagents and the experimental procedure were as same as above discussion. The catalytic oxidation to ascorbic acid at the modified electrode was exhibited in Fig 6. The oxidation peak current appeared about in 0.1 V in the range of 0.22~ −0.25V. The overpotential decreased than bare Ag electrode.

2.3.3 Ag/$(NH_4)_2MoS_4$

All of the three modified electrodes had good selectivity. But with the increase of O atoms, the stability of the electrode and effection to catalytic oxidation decreased. For $(NH_4)_2MoS_4$ modified electrode, it was fairly stable after cycled 100 times or even after experienced for two weeks. As for the $(NH_4)_2MoOS_3$ modified electrode, the chart changed after cycled 100 times and can't be experienced for long time. The situation of $(NH_4)_2MoO_2S_2$ even much worse.

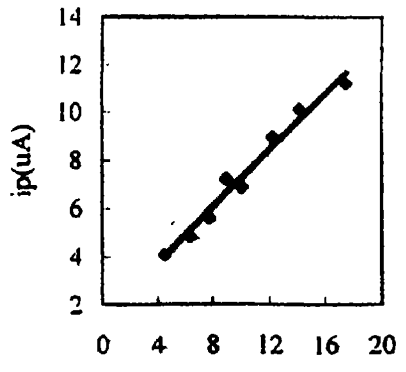

Fig 5 Plots of ip vs scan rate′ 1/2

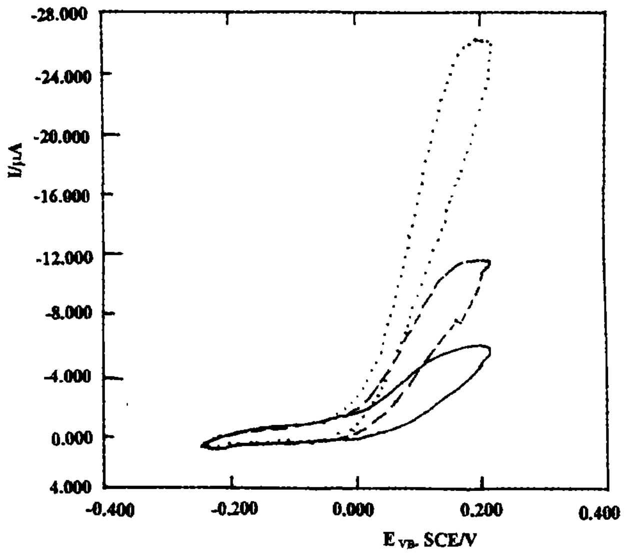

Fig 6 The catalytic oxidation to ascorbic acid by $(NH_4)_2MoO_2S_2$ modified electrode

The time for modification influenced the peak current. For $(NH_4)_2MoS_4$, it needed one minute, but the $(NH_4)_2MoOS_3$ required 2 minutes, as far as $(NH_4)_2MoO_2S_2$ was concerned, 2.5 minutes should be best. The current would be a(下转125页)

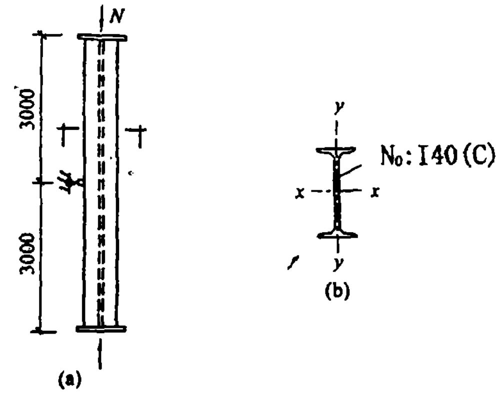

图2 例题

四、结论

本算法克服了试算法的缺点,避免了反复验算,直接算出截面尺寸大小,运算极为方便。文中仅对部分残余应力工字形截面作了初步探讨,对其它常用截面,亦可采用同样方法考虑残余应力的影响进行压柱的设计工作。

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(上接118页)little smaller before or after the right modification time.

3 Conclusion

The modified electrodes of Mo-S-Ag cluster compound films on silver surface were investigated by FT-IR, FT-Raman and XPS. The new modified electrodes were applied to the catalytic oxidation of ascorbic acid. This sort of catalytic effects can be inferred because the oxidation peak potentials of ascorbic acid moved to more negation compared with the bare Ag electrode and the oxidation peak currents increased with the increasing of ascorbic acid concentration. The overpotentials of ascorbic acid were significantly reduced. CV measurement revealed the linear relationship between the oxidation peak current and the concentration of ascorbic acid ranging among 0.001 ~ 0.06 mol/L.

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(上接122页)如英国曼彻斯特大学生物学院W.G. Bardsley博士研制的Simfit软件,用于处理化学反应动力学数据、酶反应动力学等数据的免费软件DynaFit,更多内容见CSDL的化学门户网站。

此外,还有网上化学化工新闻,网上化工贸易,网上化学化工组织如国际纯化学与应用化学联盟IUPAC、美国化学学会ACS、美国化学工程师协会AIChE、美国电化学学会(The Electrochemical Society)、基金组织等化学化工相关资源,相信随着互联网技术的不但发展,网上可供利用的化学化工资源会越来越多。

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