

Analysis of electrochemical impedance and XRD spectroscopy for complex self-assembled film on silver

Wang Yihong^{1,2} Song Wei² Gao Lijing² Ge Jie² Gu Ning¹

(¹ State Key Laboratory of Bioelectronics, Nanjing 210096, China)

(² Department of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China)

Abstract: Self-assembled monolayers (SAMs) of (3-mercaptopropyl) trimethoxysilane (3-MPT) chemisorbed on silver surfaces were chemically modified by 1-octadecanethiol to form self-assembled mixed-monolayers (SMM) and the co-polymer of N-vinylcarbazole and methyl methacrylate ester (to form complex self-assembled film (CSAF)). The oxidation resistance of these barriers on silver surfaces and some influential factors concerned processes were analyzed by electrochemical impedance spectroscopy (EIS) in a 10% NaOH aqueous solution at oxidation potential. X-ray diffraction (XRD) spectroscopy shows that the oxidation occurring on the silver surface may be restrained effectively due to the coating barrier, and CSAF(II) is the best one. Studies also reveal that oxide processes of bare silver and a series of modified silver electrodes in a 10% NaOH aqueous solution are of more than two relaxation time constants.

Key words: electrochemical impedance; X-ray diffraction; complex self-assembled multilayer; silver

Various types of self-assembled monolayers (SAMs) have been developed and many improvements and productions have been made since Sagiv reported the first real SAMs in 1980^[1]. SAMs can build up a variety of surfaces with fine chemical control by selecting different groups both in the alkyl chain and at the chain tail. But some drawbacks of SAMs are their relatively low thermal and mechanical stability, and their propensity for containing molecule-sized defects.

In order to overcome some drawbacks of SAMs as barriers, it is important that a polymer is modified on the SAMs surface. A thicker and more densely packed barrier layer to diffusion of corrosive species like O₂, OH⁻ than the SAMs is formed on the surface of the metal substrate. Accordingly, it is important that the chemical modification of monolayers is effective in protecting the noble metal surface against corrosion and oxidation, since the structure of the complex films chemisorbed on noble metal can be controlled by a functional group reaction between the SAMs and the adlayer. It is expected to reduce the drawbacks of SAMs mentioned above, and to improve the ability of anti-corrosion and anti-oxidation significantly.

In our previous work^[2], we reported the preparation method and analyzed the thickness and binding

state of complex self-assembled film (CSAF) on Ag. The CSAF was a 3-MPT SAM on the silver surface after hydrolysis chemically modified by 1-octadecanethiol (C₁₈H₃₇SH) and co-polymer composed of N-vinylcarbazole and methyl methacrylate ester. In this study, the reaction process occurring on Ag electrodes modified by CSAF was analyzed with electrochemical impedance spectroscopy (EIS) in a 10% NaOH aqueous solution, and the oxidation status on the corresponding surface was described by X-ray diffraction (XRD). No related study has been reported so far.

1 Materials and Methods

1.1 Instruments and materials

Potentiostat (CHI660, USA) with disk electrodes. X-ray diffractometer (Shimadzu, Japan) with CuK α radiation ($\lambda = 0.154\ 2\ \text{nm}$). C₁₈H₃₇SH (98%), 3-MPT (99%) and silver foil were purchased from Aldrich. A co-polymer of N-vinylcarbazole and methyl methacrylate ester was co-polymerized by 9-vinylcarbazole and methyl methacrylate in benzene at 60 °C for 4 h under a polymerization initiator. Then it was cooled to room temperature and subsequent re-precipitation from the benzene solution into petroleum ether. This procedure was repeated three times. The resultant co-polymer was dried in vacuum at ambient temperature and characterized with IR, and average molecular weight was determined to 1 000 by vapour osmotic pressure (VPO). Preparation of CSAF was the same as in our previous work^[3].

Received 2005-07-26.

Foundation item: The National Natural Science Foundation of China (Nos. 60371027, 60171005).

Biography: Wang Yihong (1962—), female, associate professor, yihongwang@seu.edu.cn.

1.2 Measurement

1.2.1 EIS measurement

A silver disk electrode (CHI Company) was used as the working electrode with a diameter of 2 mm. The electrodes were polished with emery paper down to zero grade. After ultrasonic treatment for 15 min in mini-Q and acetone in turn, the electrodes were rinsed with 100% ethanol and dried in a nitrogen stream. EIS measurements were carried out with three electrode systems in a 10% potassium hydroxide solution on exposure to air at room temperature. The working electrodes were the bare silver disk electrodes and the silver disk electrodes covered by 3-MPT, $C_{18}H_{37}SH$ SAMs, 3-MPT/ $C_{18}H_{37}SH$ self-assembled mixed-monolayers (SAMM) CSAF (I) and CSAF (II), respectively. A platinum sheet and a saturated calomel electrode (SCE), respectively. All three electrodes were connected to a potentiostat with CHI660 and EIS were measured at a series of fixed potential in the frequency range from 5×10^{-4} to 10^4 Hz for all measurements (sine signal). A small perturbing voltage to an electrochemical system was 5×10^{-3} V. All aqueous solutions were prepared from doubly distilled water and analytical grade chemicals and deaerated by bubbling N_2 for 20 min.

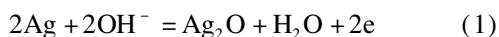
1.2.2 XRD analysis of silver oxide on bare and modified silver

XRD was carried out on an X'Pert diffractometer (Philips) equipped with a Gobel mirror under $CuK\alpha$ radiation ($\lambda = 0.1542$ nm) and parallel light. All bare Ag foil and the silver foils modified by 3-MPT SAMs hydrolyzed, SAMM, CSAF (I) and CSAF (II), respectively, were used as the X-ray diffraction identification after EIS measurement.

2 Result and Discussion

2.1 EIS analysis of adlayers on silver

There is an anodic oxidation current peak appearing over a potential range from 0.2 to 0.8 V for bare and modified silver electrodes in a sodium hydroxide aqueous solution, and the following reaction takes place at oxidation peak potentials (The saturated calomel electrode is used as the reference electrode)^[4,5]:



Those peak potentials are taken as the fixed potentials for the EIS measurement of bare silver and modified silver electrodes. We can see dark brown

Ag_2O spread over the electrode surface except the electrodes modified by CSAF(I) and CSAF(II) after EIS measurement under oxidation peak. Considering the following reaction course occurring at oxidation peak potential:

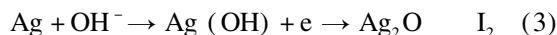
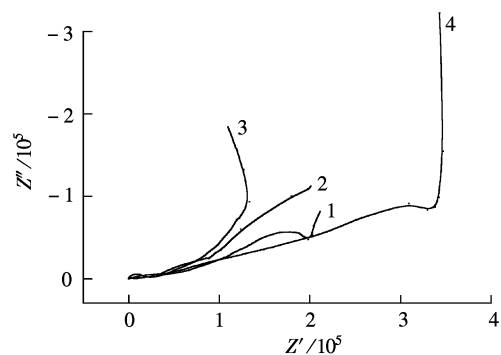


Fig. 1 and Fig. 2 show the Nyquist plots of the bare silver and modified silver electrodes at oxidation peak potentials, respectively. And there are more than two relaxation times from the Nyquist plots. It indicates that there are still other state functions affecting the oxidation process besides electrode potential E .



1—Bare Ag; 2—Hydrolyzed 3-MPT SAMs/Ag; 3—SAMM/Ag; 4—CSAF (I)/Ag electrode at oxidation peak potential

Fig. 1 Nyquist plots

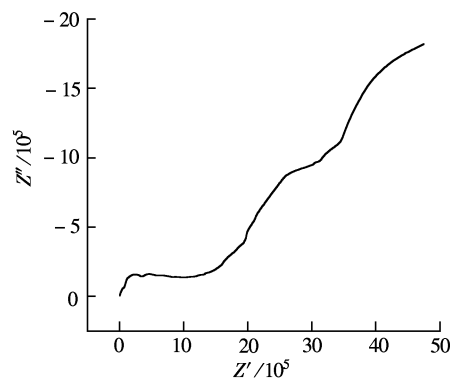


Fig. 2 Nyquist plot of CSAF(II)/Ag electrode at oxidation peak potential

There is a straight line larger than 45° on the ends of two semicircles on the Nyquist plots for bare silver (see Fig. 1). It is easy to make a conclusion that the oxidation process occurring on the bare Ag surface is of two time constants. The presence of a straight line at low frequency in the plot indicates the presence of a Warburg composition^[6,7]. That is to say, the speed of oxidation reaction is controlled by the diffusion.

The impedance response of the silver electrode modified with 3-MPT (see Fig. 1) in the lower frequency region is a semicircle instead of that of the bare

Ag electrode, similar to a response of parallel equivalent-circuit consisted of resistance and capacitance^[8]. The process of oxidation reaction is converted into the reaction process control from the diffusion process control of the bare silver electrode, which means that the resistance of oxidation reaction is increasing because there is a 3-MPT SAM barrier on the Ag surface. It can be considered that the impedance response in the lower frequency region should be affected by the modified film on reaction.

The impedance response of the silver electrode modified with SAMM (see Fig. 1) in the lower frequency region is a plot extended from the first quadrant to the second quadrant—the polarization resistance R_p is less than zero. It is indicated that the SAMM on the surface is a large resistance barrier against the oxidation reaction.

The impedance response radius for the silver electrode modified with CSAF (I) (see Fig. 1) is larger than that of the above three. Vertically upward plots, that is, the imaginary part of the impedance tending to approach infinity in the lower frequency region, indicate that the resistance of barrier against oxidation reaction is very great. The process is similar to a response of pure capacitance in an equivalent circuit^[9]. Therefore, it is concluded that there is a huge hindrance against the production of Ag_2O on the surface.

Compared to impedance responses of silver electrode modified with SAMM and CSAF (I) at oxidation peak potentials and that at their corrosion potential, it is confirmed that another time constant should be the thickness but not the coverage ratio of adlayers on the Ag surface.

The radius of the impedance plot for the silver electrode modified with CSAF (II) (see Fig. 2) aggrandizes more than ten times compared with the other four and represents the capacitance response in the lower frequency region.

It can be concluded from the above analysis that:

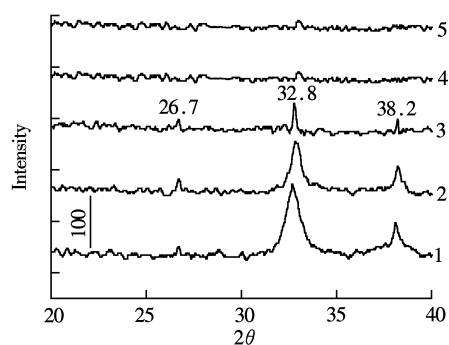
1) For the bare silver electrode and the silver electrode modified with 3-MPT, SAMM and CSAF(I), the reactants in the aqueous solution can pass through the flaws of adlayers or electrons can travel in tunnel motion through the films to reach the interface between the metal and the modified film and then produce Ag_2O . The reaction resistances increase according to this sequence: bare Ag < Ag/3-MPT SAM < Ag/SAMM < Ag/CSAF (I). CSAF (I)'s is the biggest among three modified electrodes because its greater thickness results in higher resistance.

2) For the silver electrode modified with CSAF (II), the impedance response radius is one order magnitude greater than that of the others. It is very difficult for the oxidation reaction to take place on the surface modified by this film, because of its higher density and relatively greater thickness.

3) Another major factor affecting the process at a lower frequency should be the thickness of modified film.

2.2 XRD analysis of bare silver and modified silver foils oxidized at two oxidation peak potentials

We applied XRD to characterize the chemical composition of a series of substrates after oxidizing at oxidation peak potentials. Some support can be obtained from the results of XRD for the EIS discussion of electrode processes occurring on bare silver and the surface of modified electrodes as regards the above oxidation peak potentials. It is shown in Fig. 3 that for XRD patterns of bare silver, modified silver surfaces oxidized at the oxidation peak potential. The 2θ angles of typical silver oxide (Ag_2O) are 26.7, 32.8, 38.2 and 32.3, 34.2, 37.9, respectively^[10,11]. It is shown from Fig. 3 that silver oxide is formed on the substrate surfaces and the relative intensity of silver oxide is decreased in turn as follows: bare Ag > 3-MPT SAMs/Ag > SAMM/Ag.



1—Bare Ag; 2—Ag/3MPT SAMs; 3—Ag/SAMM; 4—Ag/CSAF (I); 5—Ag/CSAF (II) at silver oxide peak potential

Fig. 3 XRD spectroscopy

There is no characteristic peak of silver oxide represented on XRD patterns for the surface modified with CSAF (I) and CSAF (II) adlayers.

3 Conclusion

According to the EIS and XRD measurements, it is concluded that the electrode processes are characterized by two time constants at the peaks of oxidation peak potentials. One in the higher frequency range is attributed to E and the other one in the lower frequency range accounts for the presence of barriers. Closely

packed and thicker Ag_2O film can be formed on the bare silver surface at the potential. All modified electrode surfaces can form Ag_2O films in different thicknesses and to various extents. The quantities of Ag_2O formed on the Ag electrode surface are decreased by the order 3-MPT SAM > SMM CSAF (I) > CSAF (II). The thickness of the barriers seems to be the primary influencing factor in affecting this oxidation process.

References

- [1] Sagiv J. Organized monolayers by adsorption. 1. Formation and structure of oleophobic mixed monolayers on solid surfaces [J]. *J Am Chem Soc*, 1980, **102**(1): 92 – 98.
- [2] Wang Yihong, Yu Qing, Zhang Yuan, et al. Self-assembled monolayers of (3-mercaptopropyl) trimethoxysilane and its mixed-monolayers with alkanethiol on silver studied by electrochemistry and X-ray photoelectron spectroscopy [J]. *Applied Surface Science*, 2004, **229**(1 – 4): 377 – 386.
- [3] Wang Yihong, Song Wei, Zhou Jie, et al. Preparation and study of complex self-assembled film as a super-thin barrier on silver [J]. *Applied Surface Science*, accepted to appear.
- [4] Teijelo M L, Vilche J R, Arvia A J. Comparative voltametric behaviour of the silver/silver oxide electrode prepared on vitreous carbon and silver substrates [J]. *J Applied Electrochemistry*, 1988, **18**(5): 691 – 698.
- [5] Fujishima Akira. *Measuring methods in electrochemistry* [M]. Translated by Chen Z, Yao J N. Beijing: Beijing University Press, 1995: 216 – 237. (in Chinese)
- [6] Liu Y H. *Electrochemical measurement technique* [M]. Beijing: National Defense Press, 1987: 160 – 170. (in Chinese)
- [7] Refaey S A M, Schwitzgebel G. Electrochemical impedance spectroscopic investigation of dissolution, passivation and pitting corrosion of Tin in Na_2CO_3 solution and the effect of Cl^- and I^- ions [J]. *Applied Surface Science*, 1998, **135**(1 – 4): 243 – 245.
- [8] Cao C, Zhang J. *Electrochemical impedance spectroscopy* [M]. Beijing: Science Press, 2002: 56 – 188. (in Chinese)
- [9] Dong S J, Che G L, Xie Y W. *Chemically modified electrodes* [M]. Beijing: Science Press, 1995: 296 – 325. (in Chinese)
- [10] Zheng X, Zhu L, Yan A, et al. Controlling synthesis of silver nanowires and dendrites in mixed surfactant solutions [J]. *J Colloid Interface Sci*, 2003, **268**(2): 357 – 361.
- [11] Waterhouse G I N, Bowmaker G A, Metson J B. Oxidation of a polycrystalline silver foil by reaction with ozone [J]. *Applied Surface Science*, 2001, **183**(3/4): 191 – 204.

银表面复合自组装膜的电化学阻抗和 X 射线衍射分析

王怡红^{1,2} 宋 伟² 高李憬² 葛 杰² 顾 宁¹

(¹ 东南大学生物电子学国家重点实验室, 南京 210096)

(² 东南大学化学化工系, 南京 210096)

摘要:银表面组装有一系列自组装膜:3-巯基-三甲氧基硅烷(3-MPT SAMs)、3-巯基-三甲氧基硅烷与十八硫醇混合自组装膜(SAMM)以及两者之上分别自组装有乙烯基吡啶与甲基丙烯酸乙酯共聚物的复合自组装多层膜(CSAF(I)和 CSAF(II)). 这些惰性膜可作为金属表面的隔绝层. 使用电化学阻抗(EIS)技术和 X 射线衍射(XRD)技术分析了表面修饰有这些自组装膜的银在 10% 氢氧化钠水溶液中的氧化阻力及其影响因素,发现自组装膜的存在不同程度地抑制了银表面的氧化反应,氧化过程存在 2 个以上时间常数.

关键词:电化学阻抗;X 射线衍射;复合自组装膜;银

中图分类号:O484. 4