

电极基底的正反馈过程对 Au/HCl 电化学振荡行为的影响^①

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摘要 当一针尖电极靠近一导电基底表面至间距与超微盘电极的直径相当时, 针尖电极上的电化学反应产物能够有效地扩散至基底表面, 并可能在其上发生电极反应使之复原为原反应物或生成其他有关物种, 从而增大针尖电极上的电化学反应电流(对应于反应物种浓度)或影响该电极过程. 本文将报道扫描电化学显微技术中的这一正反馈作用对 Au/HCl 体系的电化学振荡行为的影响. Au 电极的阳极过程一般认为由下列两步构成:



氧化膜的形成和溶解是发生振荡的一个起因, 其中 Cl^- 浓度的变化是一关键因素. 当发生振荡着的 Au 电极靠近 Pt 基底至一定间距时, 慢速的歧化反应(反应(2))产物 AuCl_4^- 扩散至 Pt 上, 导致产生大量的 Cl^- 并进一步反向扩散至 Au 电极上, 使 Au 氧化膜溶解导致反应(1)速度迅速增大, 表现出电流显著上升, 并构成新的振荡强度和时序(振荡幅度显著增加且周期有所增大). 这一反馈作用引起的 Cl^- 离子浓度的增大也可诱导振荡的发生, 使该体系在处于未发生正常振荡的电位下提前出现振荡. 实验结果表明, 对于受扩散过程控制的电化学振荡体系, 可利用电极基底的正反馈作用影响其振荡过程, 以至诱导振荡的发生.

关键词 金电极, 电化学振荡, 电极基底正反馈, 扫描电化学显微技术

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Studies of Electrochemical Oscillation of Au/HCl in Presence of "Positive Feedback" of Substrate Electrodes^①

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When a tip electrode of radius d is moved towards a conducting substrate surface to a distance of a few times of d , the product of a simple redox reaction on the tip electrode can effectively diffuse to the substrate surface and will be reversed to its original state^[1]. For a relatively complicated electrode reaction, the diffused products moving towards to the substrate may also react in other ways depending on the nature of the substrate and the applied potential. In either case, the specimen produced on the substrate surface will diffuse back to the tip electrode resulting in the increase of the steady state faradaic current or in the change of the electrode process on the tip electrode. We report here the effect of such a substrate "positive feedback" of scanning electrochemical microscopy (SECM) on the behavior of diffusion coupled electrochemical oscillation of Au/HCl system.

The anodic process of Au in HCl media is regarded in the previous studies^[2] as



The cause of the oscillation is the repetitive oxide film formation and dissolution in which the concentration of Cl^- plays an important role. Apart from the electrode potential at which oscillation can take place, the "feedback" of the substrate may also exert an additional force in changing the local concentration of Cl^- which leads to the change of oscillation amplitude and frequency. Fig. 1 gives the current oscillation before and after a Pt or a Teflon substrate was positioned near it. For comparison, the inert substrate of Teflon has also been used, it only acted as an inhibitor of the mass transfer process. It can be seen that for the Teflon substrate the oscillation behavior is essentially not changed except for a slight decrease of the baseline, while as the Pt is positioned closed to tip at 80 mV (vs Ag/AgCl), the amplitude of the oscillation current is significantly increased and there is also a slight decrease in the oscillation frequency. It is obvious that the electrode reaction on Pt is involved in some ways in the process of oscillation of Au. As the conducting substrate of Pt is approaching to the

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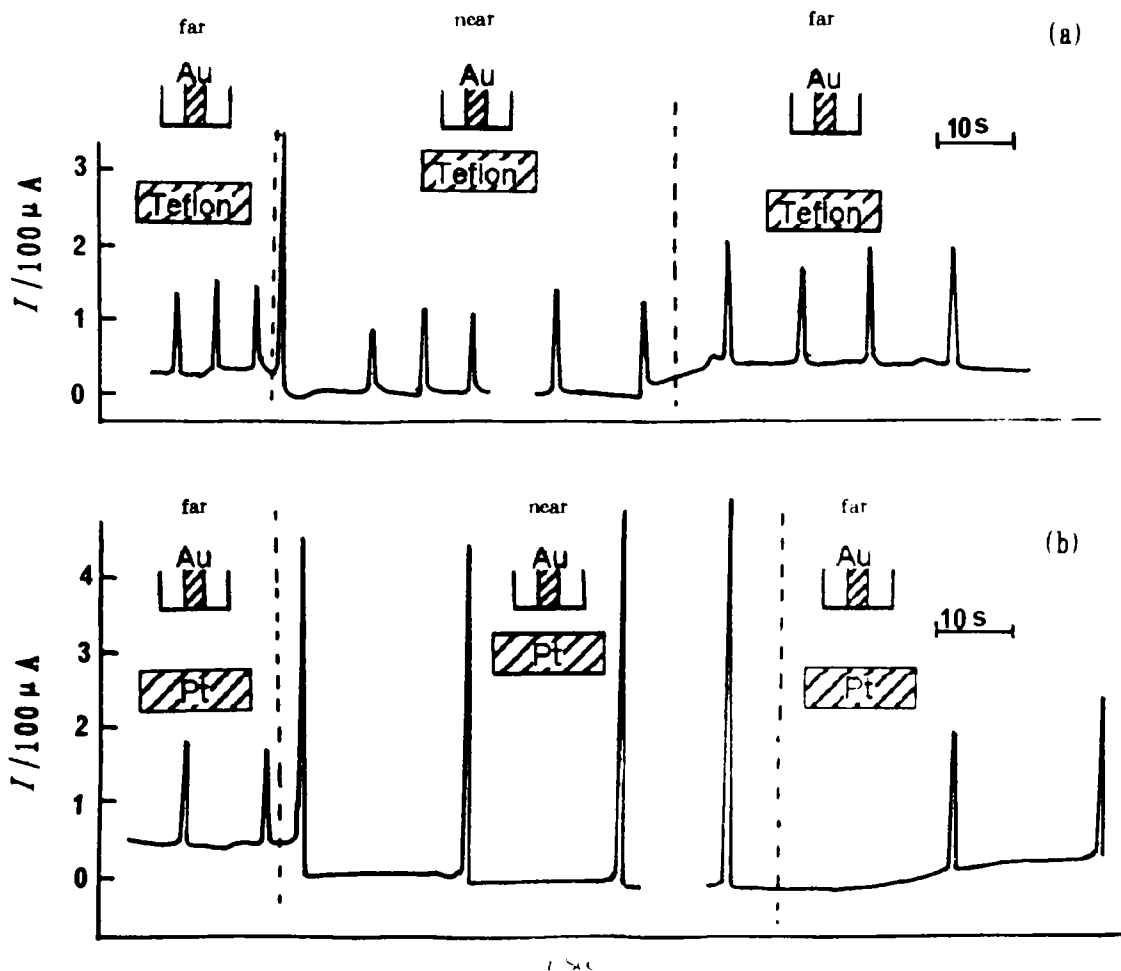


Fig. 1 Current oscillation behavior of a Au disk electrode (0.3 mm in diameter) at 1.440 V vs Ag/AgCl in 1.5 mol/L HCl solution when the Au is positioned near and far from the Teflon substrate (a) and the Pt electrode (b)

oscillating Au electrode to a certain distance, the products of reaction (2) can effectively diffuse to the Pt and the reactions may take place which produce or consume Cl^- so that the perturbation to the oscillation process sets in. Similar results can be obtained for the Pt electrode at potentials from 0~0.7 V (vs Ag/AgCl) in which the possible reactions related to the products of reaction (1) and (2) may take place. It is likely that the product $AuCl_4^-$ of the slow reaction (2) diffused to and reduced on the Pt surface to form Au, $AuCl_2^-$ and Cl^- , and the $AuCl_2^-$ may be further reduced on the Pt electrode to produce Au and Cl^- . The net reaction on the Pt can be considered as: $AuCl_4^- + 3e = Au + 4Cl^-$. The Au is deposited on the Pt and the rich amount of Cl^- is diffused to the oscillating Au electrode. The marked increase of Cl^- would increase the dissolution speed of the Au oxide film and

thus to promote the reaction (1) leading to the significant increase of the oscillation current and the formation of a new oscillation frequency and intensity.

The sudden change of Cl^- concentration due to the "feedback" effect of the substrate may also become the driving force to induce the oscillation. Fig. 2 shows that oscillation of Au in HCl solution built up at the potential earlier than where normal oscillation can take place as the Pt substrate was moved near the Au electrode. The induced oscillation disappeared after the Pt substrate was moved far from the Au electrode. The result implies that it is also possible that the "feedback" effect can further induce the oscillation of a system for which no oscillation has ever been observed.

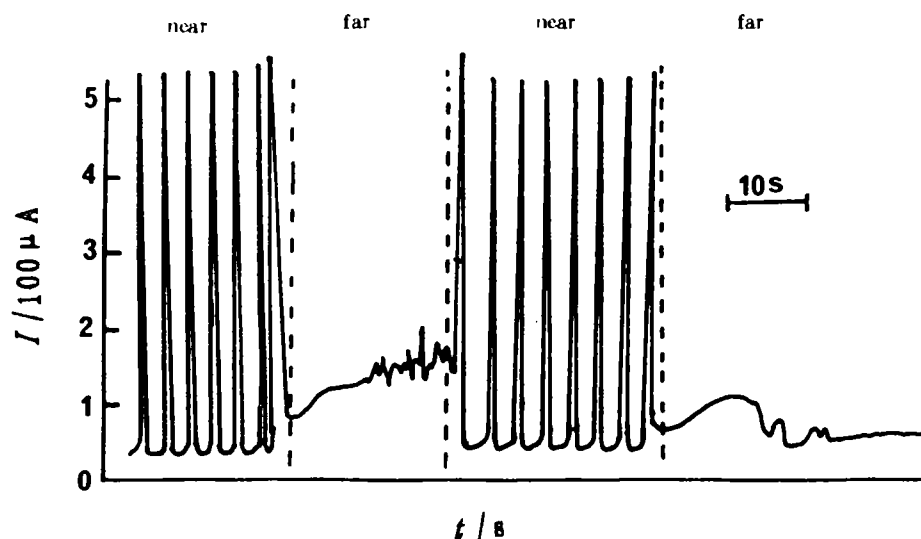


Fig. 2 Induced current oscillation of the Au electrode in 1.5 mol/L HCl at prepassivation potential

In conclusion, the results have shown that the "positive feedback" of the substrate of SECM can be used to perturb the diffusion coupled electrochemical oscillation and even to induce the oscillation process.

Key words Gold electrode, Electrochemical oscillation, positive feedback of electrode substrate, Scanning electrochemical microscopy

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