

Modulation of Electrochemical Oscillations by Specific Adsorption of Cl⁻ during the Electrooxidation of Methanol on Pt Electrode

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Abstract: Potential oscillation during the electrocatalytic oxidation of methanol can be modulated by the specific adsorption of Cl⁻ on the platinum electrode, which suppresses the electrocatalytic oxidation of methanol, and makes the cross cycle in the cyclic voltammogram become smaller and finally disappear with the increase of Cl⁻ concentration. The method is also applicable to the electrocatalytic oxidation of other small organic molecules.

Keywords: Methanol, chloride ions, specific adsorption, potential oscillation, modulation.

Oscillations during the electrocatalytic oxidation of small organic molecules have been an active area of research for more than half a century¹⁻³. Different enhancement or inhibiting effects are found by surface modification of platinum electrode using adatoms³ underpotentially deposited (*e.g.*, Pb, Sn) or irreversibly adsorbed (*e.g.*, Bi, S). Although cyclic voltammetry is a routine method employed in the study of catalytic activity of electrodes, few researchers have devoted to establish the relationship of cyclic voltammogram with electrochemical oscillations.

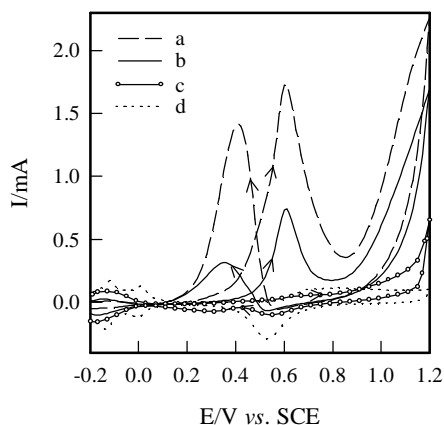
In this letter, the effect of specific adsorption of Cl⁻ on the voltammetric behavior for the electrooxidation of methanol and its connection with the potential oscillation has been studied.

Figure 1 shows the cyclic voltammograms for methanol oxidation on a platinum wire electrode (1 mm in diameter, and 8 mm in length) with different Cl⁻ concentrations in the base solution of 1 mol/L H₂SO₄. When there is no Cl⁻ (curve a), oxidation peaks appear at about 0.6 and 0.4 V during the forward and backward potential scan, respectively, from which a crossing cycle occurs, *i.e.*, the oxidation current for the backward scan is larger than that for the forward scan in a range of potentials. Poisoning CO_{ad} that forms at lower potentials can be removed at higher potentials through reaction with OH_{ad}, and the larger reverse scan current results from the oxidation of methanol on a reactivated electrode surface. The electrode surface becomes poisoned again while the potential returns into the H-adsorption range. The formation and removal of CO_{ad} consist of a pair of positive and negative feedback steps. The crossing cycle that represents the two feedback steps is a typical topology for electrochemical oscillatory systems⁴. With the increase of Cl⁻ concentration, the crossing cycle becomes smaller (curve b of **Figure 1**), and finally disappears (curve c of

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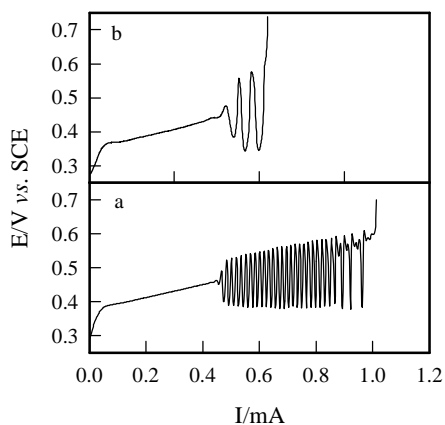
Figure 1), due to the specific adsorption of Cl^- on the Pt electrode, which inhibits the process of surface adsorption and oxidation reaction of methanol.

Figure 1 Cyclic voltammograms



(a) 1 mol/L CH_3OH +1 mol/L H_2SO_4 , (b) (a)+ 3×10^{-4} mol/L Cl^- , (c) (a)+ 3×10^{-3} mol/L Cl^- , and (d) 1 mol/L H_2SO_4 . Scan rate: 100 mV/s.

Figure 2 Potential oscillations



(a) 1 mol/L CH_3OH +1 mol/L H_2SO_4 , (b) (a)+ 2×10^{-4} mol/L Cl^- . Scan rate: (a) 2×10^{-2} , (b) 3×10^{-3} mA/s.

It is also interesting to note that the current range for potential oscillations decreases with the increase of Cl^- concentration (**Figure 2**). The oscillating frequency is varied as well. When the crossing cycle in the cyclic voltammogram vanishes, no potential oscillation occurs, which further confirms that there is a correlation of crossing cycle with electrochemical oscillations⁴.

Similar effect of specific adsorption of Cl^- on the cyclic voltammograms as well as potential oscillations has also been observed for the electrocatalytic oxidation of other small organic molecules such as formaldehyde and formic acid. So the specific adsorption of Cl^- provides a convenient way to modulate the electrochemical oscillations involving surface steps. A detailed report on the subject will be given elsewhere.

Acknowledgments

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References

1. J. Wojtowicz, *Modern Aspects of Electrochemistry*, ed. by J. O' M. Bockris, B. E. Conway, Plenum Press, New York, **1972**, 8, 47.
2. J. L. Hudson, T. T. Tsotsis, *Chem. Eng. Sci.*, **1994**, 49, 1493.
3. Beden, J. M. Léger, C. Lamy, *Modern Aspects of Electrochemistry*, ed. by J. O' M. Bockris *et al.*, Plenum Press, New York, **1992**, 22, 97.
4. Z. L. Li, Y. Yu, H. Liao, *et al.*, *Chem. Lett.*, **2000**, (4), 330.

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