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The Investigation of Oscillographic Chronopotentiometry at Silver Disk Electrode and Its Mechanism

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Abstract: A new method of oscillographic chronopotentiometry at silver disk electrode was investigated .By using it, a series of ions such as Pb, In, Cr, Tl, Bi *etc.* were determined. The detection limits are two or three orders of magnitude lower than those by oscillographic chronopotentiometry at mercury electrode. The proposed method is characterized by fine sensitivity、stable oscillogram and no mercury. The research on the mechanism of this method shows that these achievements are caused by the characterristics of silver electroxidation and electroreduction and the oscillographic chronopotentiometry (OC).

Keywords: Silver disk electrode, oscillographic determination, oscillographic chrono-potentiometry.

A.C. oscillopolarography introduced by Heyrovsky in 1941 has been developed into a new field of electroanalytical chemistry—oscillographic analysis[1]. As to the development of electrode, the change from the dropping mercury electrode (DME) to the solid electrode (the hanging mercury drop electrode or mercury film electrode) makes oscillographic analysis a real practical value[2]. Hence developing a new type of electrode is important for the progress of oscillographic analysis.

The present paper describes the investigation of oscillographic chrono-potentiometry at silver disk electrode. In this work, all experimental procedures were controlled by a microcomputer. In 1mol/L NaOH supporting electrolyte, a series of ions were determined such as Pb, In, Cr, Tl, Bi *etc*.. The results show the detection limits of the method are two or three orders of magnitude lower than those by oscillographic chronopotentiometry at mercury electrode.

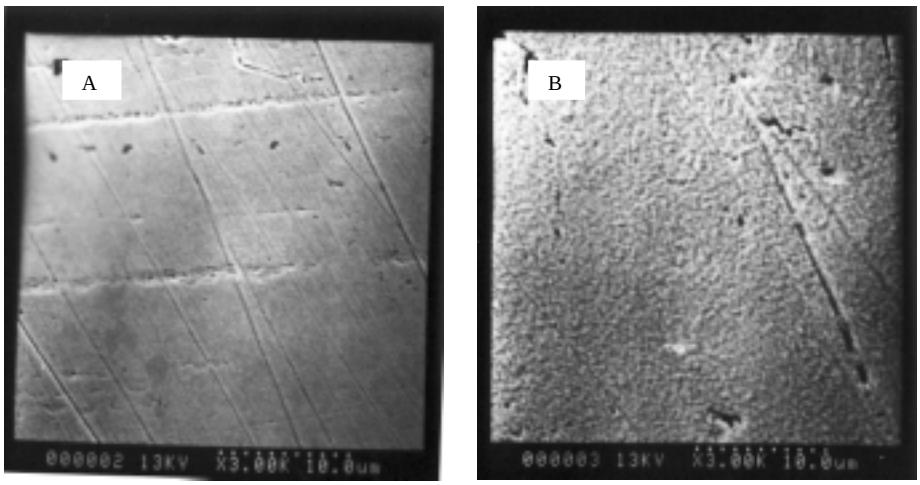
The mechanism by which oscillographic chronopotentiometry at silver disk electrode has high sensitivity and stable oscillogram was investigated in two aspects. One is method characteristic of oscillographic chronopotentiometry. The other is characteristic of electroxidation and electroreduction of silver electrode.

A.C. oscillographic chronopotentiometry is an electroanalytical method, in which a constant alternating current is passed through an electrolyte, the change of electrode potential with time is measured. The difference between a.c. oscillographic chronopotentiometry and other electroanalysis methods is that the working electrode itself undergoes reaction. The oxidation and reduction cycle on silver electrode surface results in a freshly renewed surface. So the silver electrode has advantages of solid and dropping mercury electrode. As a result, the stability of oscillogram is good. In the case

of the mercury film, like silver electrode, the oxidation and reduction cycle on mercury electrode surface takes place, but the product of depolarizer is easy to diffuse into the mercury film, which results in different states of electrode surface during each period. So the stability of oscillogram is not good.

The curve of oscillogram indicates the reduction and oxidation processes in cathodic and anodic branch. To some extent, it is similar to cyclic voltammetry. Oxidation-reduction cycle greatly changes the state of the silver surface. The smooth surface has been changed into a reformed silver surface composed of nodular deposits. The silver does not go into crystal lattice of silver, but form vertical surface. The formation of vertical surface relates to the electron transfer rate. This is best illustrated by the SEM pictures in **Figure 1**. **Figure 1**(A) is a scanning electron micrograph of polished silver surface. It is smooth except some scratches and crystal defects of silver wire itself. **Figure 1**(B) is a scanning electron micrograph of silver surface treated by oscillographic chronopotentiometry. It is apparent that the state of silver electrode surface has changed.

Figure 1 Scanning electron micrographs of polished(A) and reformed (B) silver surface



From the above evidence the following tentative explanation can be obtained. For oscillographic chronopotentiometry at silver electrode, the electrooxidation and electroreduction reaction of silver electrode are equal to a treatment for silver electrode on the spot during each period, which makes the electrode surface renewed and the number of active-groups on electrode increased. These are beneficial for the electrode performance. So the sensitivity can be increased greatly.

References

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