Analytical Applications and Catalytic Activities of Electrodeposited Thallic Oxide Films

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Thallic oxide (Tl_2O_3) were electrodeposited onto indium tin oxide (ITO) conducting glass substrates in alkaline solutions. It has a high catalytic activity for the anodic oxidation of sulfite (SO_3^{2-}) and thiosulfate ($S_2O_3^{2-}$) anions. Also it can be used for electroanalysis of nitrite ions (NO_2^-) with an excellent stability and a detection limit of 4.0×10^{-6} mol/dm^3.

Recently, there is an increasing interest in the electrodeposition of Tl_2O_3 film with respect to preparation of Tl-Pb oxide and Tl_2O_3 superllatices,[1-3] and high temperature superconductor films.[4, 5] Its electrocatalytic behavior has rarely explored so far except its catalytic effect on the ferrocyanide/ferricyanide redox couple.[6, 7] In our previous studies,[8] it is found that the obtained Tl_2O_3 film is amorphous at low electrodepositing current densities, while at high current densities it is polycrystalline. Furthermore, the polycrystalline film has a lower resisitivity than the amorphous one. A low resistivity of 3.2×10^{-4} Ω·cm of the polycrystalline film can be obtained when the Tl_2O_3 was electrodeposited on the ITO surface at an electrodeposition current density of 20 mA/cm^2 in an aqueous solution of 1.00 mol/dm^3 KOH containing 0.50 mol/dm^3 thallous acetate. In the present studies, the above polycrystalline Tl_2O_3 film with a resistivity of 3.2×10^{-4} Ω·cm is used. It is found that the electrodeposited polycrystalline Tl_2O_3 film has a higher activity for the anodic oxidation of the SO_3^{2-} ions than platinum and ITO conducting glass. In addition, the electroanalytical determination of NO_2^- using the electrodeposited Tl_2O_3 film electrode is explored. All electrode potentials are referred to a saturated calomel electrode (SCE). The square resistance of the ITO conducting glass is 40 Ω. All experiments are performed at 25 °C.

In the voltammetric scan experiment, it was found that the ITO had no activity for the anodic oxidation of NO_2^-. When the Tl_2O_3 film-coated ITO substrate was used, the anodic current increased remarkably and a well defined current peak centred at +0.98 V(vs.SCE), demonstrating that the Tl_2O_3 film has a high catalytic activity for the anodic oxidation of NO_2^-. The voltammograms at different concentrations of NO_2^- are shown in Figure 1. When i_p, the anodic peak current density (back-ground-subtracted), was plotted against C, the concentration of NO_2^-, a straight line was obtained and shown in Figure 2. The good linear relationship between the peak current and the concentration of NO_2^- demonstrates a sensor application of the Tl_2O_3 film for the electroanalysis of NO_2^-. The stability and the reproducibility of the Tl_2O_3 film were examined from the following three aspects. First, when the Tl_2O_3 film was stored in a 4.00 mol/dm^3 $NaNO_2$ solution for 120 h, no surface change was observed. In addition, no change of the peak current was found after ten days of the immersion of the Tl_2O_3 film in a 0.500 mol/dm^3 $NaNO_3$ solution containing 1.00×10^{-3} mol/dm^3 $NaNO_2$. These results demonstrate that the Tl_2O_3 film is very stable in NO_2^-–containing

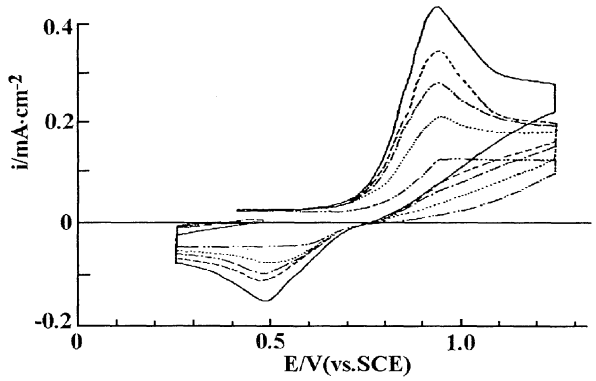

Figure 1. Voltammograms of the first scan at Tl_2O_3 film-coated ITO electrodes in a 0.500 mol/dm^3 $NaNO_3$ solution containing different concentrations of NO_2^- ions.
Scan rate: 50 mV/s;Concentration of NO_2^- ions (mol/dm^3) × 10^{-3}: (— · · — · ·) 0.20, (.....) 0.40, (— · — ·) 0.60, (- -) 0.80, and (____) 1.00.

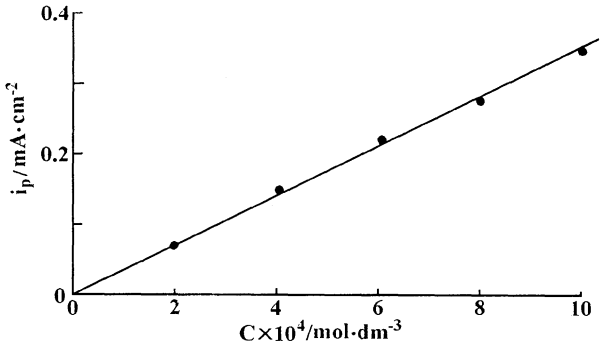

Figure 2. Linear relationship between anodic peak current and concentration of NO_2^- ions.

$NaNO_3$ solutions. Second, after 30 times of repeated linear voltammetric scans were performed on the Tl_2O_3 film electrode in a 0.500 mol/dm^3 $NaNO_3$ solution containing 1.00×10^{-3} mol/dm^3 $NaNO_2$, the Tl_2O_3 film was kept in the same solution for 14 h. Then 20 times of repeated linear voltammetric scan were performed. The time interval between two adjacent scans was 5 min. For these 50 times of repeated linear voltammetric scans, the relative average deviation of the peak current was 2.7% which demonstrated a good stability and a good reproducibility of the Tl_2O_3 film during the repeated voltammetric scan experiments. Third, the Tl_2O_3 film was electrodeposited on the ITO substrate and the linear voltammetric scan was performed in a 1.00×10^{-3} mol/dm^3 $NaNO_2$ +0.500 mol/dm^3 $NaNO_3$ solution

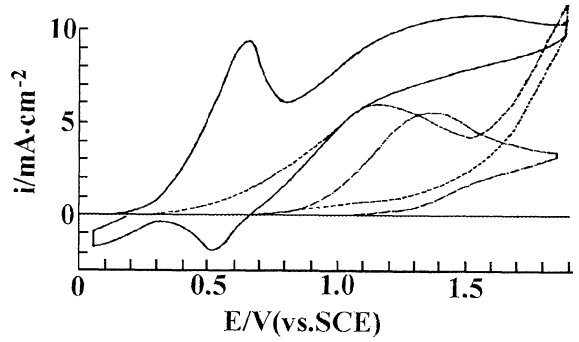

Figure 3. Voltammograms for Pt(----), ITO (— · — ·), and Tl_2O_3 film-coated ITO(—) electrodes in a 0.10 mol/dm^3 Na_2SO_3 electrolyte.
Scan rate: 43 mV/s.

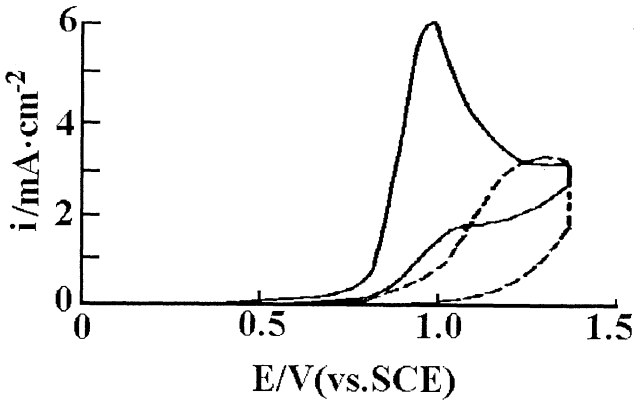

Figure 4. Voltammograms for Pt(---) and Tl_2O_3 film-coated ITO (—) electrodes in 0.010 mol/dm^3 NaOH electrolyte containing 0.010 mol/dm^3 $Na_2S_2O_3$ electrolyte.
Scan rate: 43 mV/s.

For 13 times of such parallel experiments, the relative averaged deviation of the peak current was only 1.6% which demonstrates an excellent reproducibility of the electrodeposition of the Tl_2O_3 film. The selectivity of the the Tl_2O_3 film for the electroanalysis of NO_2^- was studied by linear scan voltammetry in a 1.00×10^{-3} mol/dm^3 $NaNO_2$ +0.500 mol/dm^3 $NaNO_3$ solution containing 0.100 mol/dm^3 of the species to be examined. No interference was found for NO_3^-, SO_4^{2-}, Cl^-, ClO_4^-, $Fe(CN)_6^{3-}$, NH_4^+, Na^+, and K^+. However, Fe^{2+}, $Fe(CN)_6^{4-}$, $S_2O_3^{2-}$, and SO_3^{2-} interfered with the electroanalysis of NO_2^- due to their concurrent anodic oxidation on the Tl_2O_3 film electrode.

Figure 3 shows the cyclic voltammograms for the oxidation of SO_3^{2-} at Pt, ITO, and Tl_2O_3 film-coated ITO electrodes. Two anodic peaks were observed in the case of the Tl_2O_3 film electrode. The first centred at +0.65 V and the second centred within a broaden range. For the Pt and the ITO electrodes, only one anodic peak was observed which centred at 1.17 V and 1.38 V, respectively. The onset potential for the Tl_2O_3 film-coated ITO electrode was +0.10 V which was about 0.18 V and 0.55 V more positive than those for the Pt and the ITO electrodes respectively, indicating that the anodic oxidation of the SO_3^{2-} ions on the Tl_2O_3 film-coated ITO electrode is much easier than on Pt and ITO. In addition, the peak current density of the Tl_2O_3 film-coated ITO electrode was larger than those of the Pt and the ITO, demonstrating that the anodic oxidation process of the SO_3^{2-} ions goes faster on the Tl_2O_3 film-coated ITO electrode than on Pt and ITO.

Figure 4 shows the cyclic voltammograms for the oxidation of $S_2O_3^{2-}$ at Pt and Tl_2O_3 film-coated ITO electrodes. The onset potential for the Tl_2O_3 film-coated ITO electrode was +0.50 V which was 0.27 V more negative than that for the Pt electrode. In addition, the peak current density of the Tl_2O_3 film-coated ITO electrode was much higher than that of the Pt. These results demonstrated a higher catalytic activity of the Tl_2O_3 film than those of Pt and ITO for the anodic oxidation of the $S_2O_3^{2-}$ ions.

In summary, the electrodeposited Tl_2O_3 film has a good stability and a good reproducibility for the determination of NO_2^-. It also does not passivate during the anodic process. The i_p-C straight line of the Tl_2O_3 film electrode was approximately the same as that of a qPVP/$IrCl_6^{2-,3-}$-modified glassy carbon electrode,[9] demonstrating a sensor application of the Tl_2O_3 film to the electroanalysis of NO_2^-. The detection limit was 4.0×10^{-6} mol/dm^3. In addition, the electrodeposited Tl_2O_3 film has a higher activity than Pt for the anodic oxidation of the SO_3^{2-} and the $S_2O_3^{2-}$ ions. This results is important for electroanalysis and elimination of the SO_3^{2-} and the $S_2O_3^{2-}$ ions in the industrial waste water. Further studies on the stability and the reproducibility of the electrodeposited Tl_2O_3 film electrode in the determinations of SO_3^{2-} and $S_2O_3^{2-}$ ions are being carried out in our laboratory.

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