Determination of Dopamine in the Presence of Ascorbic Acid on the IrO₂-Ta₂O₅ Type DSA Electrode

Yang LIU, Zhi Ying LI, Jing Hong LI*

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022

Abstract: IrO₂/Ta₂O₅ (70%: 30%, molar ratio) electrodes (ITEs) were prepared by the thermal decomposition method. Typical "mud-cracked" surface and surface enrichment of Ta were observed. The determination of dopamine (DA) was carried out in the presence of ascorbic acid (AA). The detection limit of DA was 5×10^{-5} mol/L without the interference of AA.

Keyword: Dopamine, ascorbic acid, determination, DSA.

Dimensional stable anodes (DSAs), which can generate an active hydroxyl radical and active chloride species to destroy organic waste and water with low overpotential and long life-time, were widely used in the field of chlorine, oxygen production, metal electrowinning and electro-organic synthesis¹⁻⁴. The active materials of the DSAs enable the electrical charge transport between the base metal and the electrode/electrolyte interface and have high chemical, electrochemical stability and the ability to catalyze the desired electrochemical reaction. However, no work has been reported on the application to the electrochemical analysis of DSAs. Dopamine (DA) is one of the most important neurotransmitters and plays a significant role in the function of central nervous, renal and hormonal systems⁵. A common problem of electrochemical analyses of DA is the lack of selectivity due to the presence of interfering compounds such as ascorbic acid (AA), whose redox peaks are very close to DA's on the ordinary electrodes ⁶⁻⁸. In this work, the IrO_2 -Ta₂O₅ (70:30, mol) electrodes (ITEs), which have been verified as the best combination in the recent commercial applications owing to their good electrocatalytic activities and high stability, were prepared by thermal decomposition method and characterized by XPS and SEM. The electrooxidation and determination of DA in the presence of ascorbic acid on the ITEs were also investigated.

First, the titanium was sandblasted and placed in hot alkaline solution for 30 min. After that, the substrate was washed with deionized water and etched in hot (70 °C) 3 mmol/L HCl solutions for 30 min and washed with deionized water again. The precursor was prepared by dissolving H₂IrCl₆·xH₂O (x≈4) and TaCl₅ with mole ratio of 7:6 in an ethanol–isopropanol mixture. Then, the substrates were painted with the precursor by

^{*} E-mail: lijingh@ciac.jl.cn

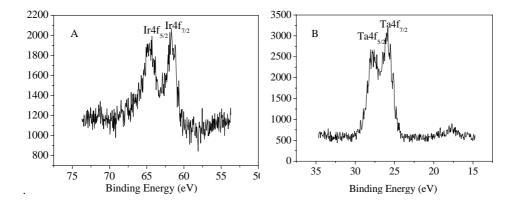
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brushes. After being dried at 80 °C, the titanium substrates were heated at an annealing temperature of 450 °C for 15 min. The entire procedure was repeated seven times. Finally, the samples were heated at the same annealing temperature for 1h.

Figure 1 shows the XPS spectra of Ta (A) and Ir (B) of the electrodes. The bonding energies of Ir $4f_{7/2}$ at 61.5 eV and Ta $4f_{7/2}$ at 25.9 eV indicated that they existed in the forms of IrO₂ and Ta₂O₅. The molar ratio of Ir and Ta calculated as 23/77 based on the peaks of Ir $4f_{7/2}$ and Ta $4f_{7/2}$ indicated the surface enrichment of Ta, which was accordant with that of Roginskaya ⁹. A typical "mud-cracked" morphology for DSAs prepared by thermal decomposition method was observed by the SEM micrograph.

Electrooxidation of DA was carried out on the ITEs in the different pH buffer solutions. As the pH increased, the anodic peak negatively moved for the catalysis of ITEs. Figure 2 shows the effect of pH on the oxidation current of 0.5 mmol/L DA. It was found that the largest current response was occurred in the solution with pH 5.00. So in the following experiments, the solution with pH 5.00 was selected. Figure 3 shows the cyclic votammograms of blank (a), DA (b), AA (c) and the mixture of DA and AA (d) in the Britton-Robinson buffer solution. DA showed an anodic peak at 500 mV and a cathodic peak at 180 mV in curve b. In addition, the anodic peak moved positively and the cathodic peak moved negatively with the increase of scan rate, which showed a typical quasi-reversible process. A large background current was observed for the capacitive character of the IrO₂ type electrodes. Furthermore, the relationship of the anodic peaks of DA and pH was investigated. A regular variation of oxidative potential/pH shift was got and the linear dependence exhibited a slope of ca. 60 mV per unit of pH. As for AA, there is no obvious redox peak to be observed in curve c. In curve d, the anodic peak was nearly consistent with that of DA in curve b. From the above results, we concluded that AA had nearly no influence on the detection of DA. The detection limit of DA in the presence of AA on the ITEs was 5×10^{-5} mol/L.

 $\label{eq:Figure 1} \begin{array}{ll} XPS \mbox{ spectra of } Ir \mbox{ (A) and } Ta \mbox{ (B) on the } IrO_2/Ta_2O_5 \mbox{ type } DSA \mbox{ electrodes annealed at } 450 \mbox{ °C by thermal decomposition method} \end{array}$



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Figure 2 The effect of pH on the oxidation current of 0.5 mmol/L DA

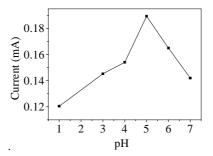
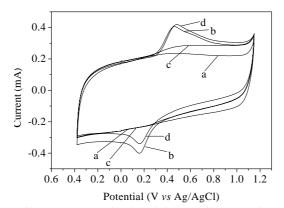


Figure 3 Cyclic votammograms of DA and AA at the IrO₂/Ta₂O₅ type DSA electrode in Britton-Robinson buffer solution (pH=5.00).



a, blank, b, 0.5 mmol/L DA, c, 1 mmol/L AA, d, 0.5 mmol/L DA and 1 mmol/L AA. Scan rate, 100 mV/s

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