

Studies of surface alloy as high efficient electrocatalyst for glyoxylic acid synthesis

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The organic electrosynthesis is of advantage in many aspects, such as high selectivity and no pollution to environment. In recent years, with more social attention focused on the environment and energy problems, the organic electrosynthesis has become an important part in the industry of green synthesis. The synthesis of glyoxylic acid by means of electro-reduction of oxalic acid has played an important role not only in fine chemical industry, spice synthesis and pharmaceutical chemistry, but also in the fundamental studies of electrocatalysis. Lead, carbon and other materials are often used as cathodes for this synthesis. However, the problem of high overvoltage is encountered with these materials. For example, the reduction of oxalic acid on lead cathode takes place at potentials below -1.2 V (SCE) ^[1], which leads to a large consumption of energy. In addition, the generation of by-products (mainly glycolic acid^[2]) and the corrosion of lead cathode under conditions of high current density^[3] cause also many difficulties in purifying the products. As a consequence, to develop new electrocatalysts of high selectivity and activity become a key step in advancing the industrial process of electrosynthesis of glyoxylic acid. In the present paper, three kinds of electrode of surface alloy (Pb-Pt/GC, Sb-Pt/GC and Pb-Sb-Pt/GC) were prepared and tested for the reduction of oxalic acid, which has thrown a new light into design and preparation of electrocatalyst of high performance for glyoxylic acid synthesis.

1 Experimental

Two types of electrochemical cell, an H-type cell and an undivided cell, were used in experiments. The compartments of H-type cell are separated by a glass frit. A saturated calomel electrode (SCE) and a platinum foil were used in both cells as reference and auxiliary electrode, respective-

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ly. To eliminate the interference of K^+ and Cl^- from SCE reference electrode, the electrochemical cell was separated from the compartment of reference electrode by a solution bridge. The electrodes of surface alloy were prepared through the following steps: 1) polishing glassy carbon (GC: $\varnothing = 8.0$ mm) at first with 4 ~ 6 # Jing Xiang sand paper and then with Al_2O_3 polishing powder of size $1 \sim 0.3 \mu$. The surface of GC was cleaned afterwards through an ultrasonic bath; 2) depositing galvanostatically platinum layer of different thickness by controlling the charge passed; 3) transferring this platinized glassy carbon into the solution containing different metal ions (Pb^{2+} , Sb^{3+} , or both), and by setting windows of potential cycling to get surface alloy of different composition and structure. All solutions were prepared from A. R reagents and Millipore water supplied from a Milli-Q Lab system. The data were acquired and processed by a micro-computer interfaced with a XHD-II potentiostat. The potentials reported in this paper were referred to SCE scale and the potential sweep rate was at $50 \text{ mV} \cdot \text{s}^{-1}$ for all experiments. The experiments were carried out at room temperature.

2 Results and discussion

2.1 Preparation and characterization of surface alloy electrodes

The voltammograms of deposition of Pb^{2+} or Sb^{3+} ions on a platinized glassy carbon (Pt/GC) are shown in Fig. 1. From Fig. 1a a reduction peak is observed at -0.2 V and an oxidation peak appears at around -0.45 V, which may be attributed respectively to the reduction of Pb^{2+} and the oxidation of deposited Pb. We observe also a pair of redox peaks near -0.08 V and 0.22 V from this voltammogram. In order to ascertain the origin of this pair of peaks, the electrode of Pt/GC after deposition of Pb, i. e., the surface alloy electrode of Pb-Pt/GC was rinsed with Millipore water and transferred to a pure $0.1 \text{ mol} \cdot \text{L}^{-1} \text{HClO}_4$ solution. In the voltammogram recorded the peaks near -0.52 and -0.45 V disappeared, and the redox pair of peaks at -0.08 and 0.22 V remained. In comparison with a cyclic voltammogram of Pt/GC electrode in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{HClO}_4$ no peaks appeared at -0.08 and 0.22 V, it is evident that the pair of peaks at -0.08 and 0.22 V is due to the reduction and oxidation of surface alloy of Pb-Pt. In the case of Sb^{3+} (Fig. 1b) the de-

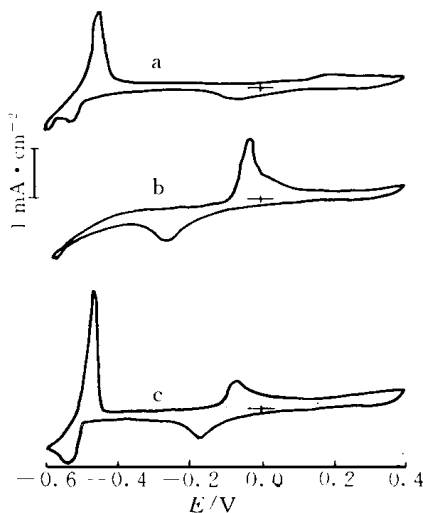


Fig. 1 Cyclic voltammogram curve of Pt/GC
 a. $10^{-3} \text{ mol} \cdot \text{L}^{-1} \text{Pb}^{2+} + 0.1 \text{ mol} \cdot \text{L}^{-1} \text{HClO}_4$
 b. $10^{-3} \text{ mol} \cdot \text{L}^{-1} \text{Sb}^{3+} + 0.1 \text{ mol} \cdot \text{L}^{-1} \text{HClO}_4$
 c. $10^{-3} \text{ mol} \cdot \text{L}^{-1} \text{Pb}^{2+} + 10^{-3} \text{ mol} \cdot \text{L}^{-1} \text{Sb}^{3+} + 0.1 \text{ mol} \cdot \text{L}^{-1} \text{HClO}_4$

position and dissolution current peak are located around -0.25 and -0.05 V. When the solution contains both Pb^{2+} and Sb^{3+} ions, the voltammogram (Fig. 1c) displayed clearly two pairs of current peak. One located near -0.18 and -0.06 V, due to the reduction of Sb^{3+} and the oxidation of Sb, and the other at around -0.52 and -0.45 V corresponds to the reduction of Pb^{2+} and the oxidation of Pb. It may be noted that from all voltammograms in Fig. 1 that the charge integrated in the negative going potential sweep (NGPS) is always larger than the charge calculated in the positive going potential sweep (PGPS), implying that in each potential cycling, a small quantity of metal (Pb, Sb) was deposited onto the surface of Pt/GC electrode. So, by controlling the number of potential cycling we may control the quantity of Pb and Sb deposited on Pt/GC surface. The electrodes of different surface alloy (Pb-Pt/GC, Sb-Pt/GC and Pb-Sb-Pt/GC) prepared in this experiment were rinsed by pure water and transferred to another cell for further study.

2.2 Electrocatalytic effects of different surface alloy electrodes for synthesis of glyoxylic acid via the reduction of oxalic acid

The voltammograms recorded with three kinds of surface alloy electrode prepared in 2.1 in a solution containing $0.2 \text{ mol L}^{-1} \text{ C}_2\text{H}_2\text{O}_4$ are displayed in Fig. 2. We measured that, at potential of -0.5 V, the reduction current of oxalic acid on Pb-Pt/GC, Sb-Pt/GC and Pb-Sb-Pt/GC is respectively at -0.5 , -2.5 and $-3.6 \text{ mA} \cdot \text{cm}^{-2}$, which are much larger than the current of hydrogen evolution in pure HClO_4 solution on the same electrode. From these voltammograms we can measure also the onset potential of reduction of oxalic acid, which is respectively at -0.52 , -0.45 and -0.4 V for Pb-Pt/GC, Sb-Pt/GC and Pb-Sb-Pt/GC electrodes. To compare the value of -1.1 V for the reduction of oxalic acid on a Pb cathode^[11], the electrocatalytic effect of these three kinds of surface alloy electrode is evident. The reduced products can be oxidized at potentials above 0.0 V and yielded a peak at about 0.25 V as shown in the figure. For the same lower limit of potential sweep, the intensity of current of the anodic peak due to the oxidation of reduced oxalic acid on Pb-Pt/GC, Sb-Pt/GC and Pb-Sb-Pt/GC electrodes is 0.4 , 0.6 and $1.0 \text{ mA} \cdot \text{cm}^{-2}$, respectively. These results demonstrate that the Pb-Sb-Pt/GC electrode is the most active one among the three electrodes prepared, since

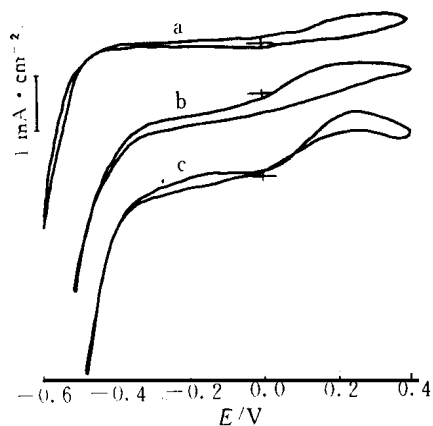


Fig. 2 Cyclic voltammogram curve of surface alloy electrode in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HClO}_4 + 0.2 \text{ mol} \cdot \text{L}^{-1} \text{ C}_2\text{H}_2\text{O}_4$

a. Pb/Pt/GC
b. Sb/Pt/GC
c. Pb/Sb/Pt/GC

it gives the highest onset potential for $C_2H_2O_4$ reduction and the largest current density for the oxidation of the reduced products. The electrocatalytic activity of these three types of surface alloy electrode may be thus arranged in an order of $Pb-Sb-Pt/GC > Sb-Pt/GC > Pb-Pt/GC$.

2.3 The identification of reduced products of oxalic acid by infrared spectroscopy

The IR spectrum of electrolytic solution after 12 hours reduction of oxalic acid on a $Pb-Sb-Pt/GC$ electrode (Fig. 3b) displayed mainly four peaks of absorption: 1700 cm^{-1} , 1315 cm^{-1} , 1233 cm^{-1} and 1108 cm^{-1} . In comparison with the spectra of oxalic acid (Fig. 3a) and that of glyoxylic acid (Fig. 3c), these four peaks can be assigned as follows: $\nu_{C=O}$ of $C_2H_2O_4$ or $C_2H_2O_3$ (1700 cm^{-1}); ν_{C-C} of $C_2H_2O_3$ (1315 cm^{-1}); ν_{C-C} of $C_2H_2O_4$ (1233 cm^{-1}); the absorption of $HClO_4$ (1108 cm^{-1}). These results proved that the electrolytic solution of reduction of oxalic acid may contain a mixture of oxalic acid ($C_2H_2O_4$) and glyoxylic acid ($C_2H_2O_3$), and illustrated that the main product specie of $C_2H_2O_4$ reduction on $Pb-Sb-Pt/GC$ electrode is glyoxylic acid.

3 Conclusions

In the present studies, we have prepared three types of surface alloy electrode, and demonstrated that these electrodes possess a high activity towards the electro-synthesis of glyoxylic acid via the reduction of oxalic acid. The order of activity of these surface alloy electrode has been arranged as $Pb-Sb-Pt/GC > Sb-Pt/GC > Pb-Pt/GC$. Further work will be emphasized on studies of the structure of these surface alloy electrocatalysts and on the mechanism of the reduction of oxalic acid.

Keywords Glassy carbon, Surface alloy electrode, Oxalic acid, Glyoxylic acid

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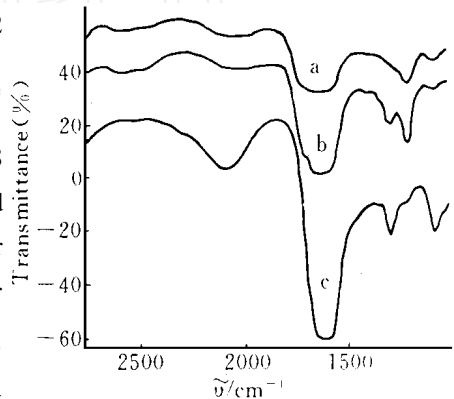


Fig. 3 Infrared spectra of electrolytic solution of oxalic acid.

- a. $0.6\text{ mol}\cdot\text{L}^{-1}\text{ C}_2\text{H}_2\text{O}_4 + 0.1\text{ mol}\cdot\text{L}^{-1}\text{ HClO}_4$
- b. Solution after 12 hrs of electrolysis on $Pb-Sb-Pt/GC$ electrode
- c. $0.1\text{ mol}\cdot\text{L}^{-1}\text{ C}_2\text{H}_2\text{O}_3 + \text{mol}\cdot\text{L}^{-1}\text{ HClO}_4$

用于乙醛酸电合成的高效表面合金电催化剂研究

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摘要 运用电化学方法, 研制了三种表面合金 (Pb-Sb-Pt/GC, Sb-Pt/GC, Pb-Pt/GC) 电催化剂, 发现在草酸还原生成乙醛酸的电有机合成中这些表面合金电催化剂有较高的活性, 其起始还原电位分别比在 Pb 阴极上 (-1.1 V) 提前了 0.48 ~ 0.70 V。这三种表面合金电催化剂的活性次序为: Pb-Sb-Pt/GC > Sb-Pt/GC > Pb-Pt/GC。红外光谱结果表明, 在这些表面合金电极上草酸还原产物主要为乙醛酸。

关键词 玻碳, 表面合金电极, 草酸, 乙醛酸