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Short communications

The Kinetics for the Electrochemical Synthesis of Adipic Acid

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A new method of synthesis of adipic acid from cyclohexanol was reported. The electrochemical oxidation process was investigated by polarization curve by taking Ti/SnO_2+Sb_2O_3/PbO_2 as anode and $Cr_2O_7^{2-}/Cr^{3+}$ as indirect oxidant. The influence of Ag^+ on the electro-oxidation progress of Cr^{3+} was discussed. The results showed that Ag^+ acted the effective catalyst in the oxidation of Cr^{3+}. The mechanism of indirect electrochemical oxidation of adipic acid was suggested and checked, and step 1 was confirmed to be as the reaction controlled step. The electro-oxidation mechanism of cyclohexanol or cyclohexanone can provide a theoretical foundation for the industrial production of adipic acid.

Keywords: adipic acid, electrochemical oxidation, cyclic voltammetry, mechanism

1. INTRODUCTION

Adipic acid (AA) is of great importance commercially in that it is used in the manufacture of nylon 6,6, which, in turn, is extensively used in many products such as tire reinforcements, adhesives, upholstery, specialty foams, carpet fibers and several items of clothing[1,2]. Adipic acid is often synthesized by HNO_3 [3] or hydrogen peroxide [4-6] as oxidant in technical processes, which is greatly harmful to environment and is very expensive process. In the author's opinion, the electrochemical method provides a versatile means for the selective reduction and oxidation of organic compounds. The electro-organic synthesis has many advantages, such as normal temperature and pressure, easy control and so on. The importance of an electrochemical synthesis lies not only in the selectivity of the reaction, but also in the activity of electrons at the electrode surface. Hence, since the electrons are reagent free, pollution of the environment by spent reagents can be avoided [7], and $Cr_2O_7^{2-}/Cr^{3+}$ is a common oxidant pair in the electrochemical synthesis [8]. This paper reports a new method to synthesize adipic acid by electro oxidation of cyclohexanol with $Cr_2O_7^{2-}/Cr^{3+}$ as indirect oxidant [9]. The mechanism for this electrochemical synthesis was also investigated. Our aim is to provide a theoretical foundation for the industrial production of adipic acid.

2. EXPERIMENTAL

2.1 Instruments and reagents

VMP3-Multi potentiostat electrochemical station (Princeton Applied Research Instruments, Inc., USA) was used to measure cyclic voltammograms (CV). All reagents were analytical grade. The solutions were prepared with fresh double-distilled and deionized water.

2.2 Electrochemical experiments

2.2.1 Preparation of anode

The detail of the preparation method of the anodes can be found in Refs. [8]. A 7cm×1cm×1cm titanium plate was used as the substrate, the titanium plate was treated by sandblasting, followed by a chemical treatment in hot 5% (V/V) NaOH solution for 60 min and in hot 10% (V/V) oxalic acid for 60min, respectively. Finally, the support was washed with purified water and dried at 120℃.

The SnO_2 +Sb_2O_3 coating on the support was prepared with a 10 mL *n*-butyl alcohol solution containing 4 g $SnCl_4 \cdot 5H_2O$ and 0.332 g $SbCl_3$. The solution was quantitatively spread on the pretreated support and the coating was initially treated at 100℃ for 10 min. And then it was annealed at 450℃ for 10 min. This procedure was repeated 10 times, and finally the anode was annealed 500℃ for 60 min.

At last, PbO_2 was electrodeposited on the above substrate in acidic solution. The acidic bath solution for depositing PbO_2 layer was composed of the following chemicals: $Pb(NO_3)_2$:160.0-170.0 $g \cdot L^{-1}$, HNO_3: 3.0-5.0 $g \cdot L^{-1}$ (pH 1.0-2.0) and a little $Cu(NO_3)_2$.

2.2.2 CV experiment

All electrochemical experiments were performed in a conventional three-electrode cell system, more specifically, taking the Ti/SnO_2+Sb_2O_3/PbO_2 as anode (the working electrode), Ni cathode as the counter electrode, and SCE as the reference electrode. The anolyte was 0.2 M $Cr_2(SO_4)_3$ (50mL) solution containing Ag_2SO_4, $(NH_4)_2SO_4$ and H_2SO_4. The cyclic voltammetry was recorded on a adipic acid was VMP3 Multi potentiostat at ambient temperature.

3. RESULTS AND DISCUSSION

3.1 The reaction mechanism of the electrode

F.I. Danilov[8] studied the catalytic activity of the MnO_2 electrode used for the oxidation reaction of Cr(III) to Cr(VI). Under the action of OH· free radical from the anodic ionization of water the Cr(III) was oxidized to Cr(VI). Then the Cr(VI) oxidized corresponding organic compound on the electrode surface. The above is the reaction mechanism on the catalytic action of indirect oxidant. According to the thought, the reaction mechanism of the electrode may be suggested as the following [10--13] :

1. $Ag^+ - e^- \rightarrow Ag^{2+}$

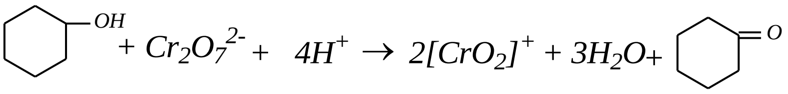
2. $Cr^{3+} + Ag^{2+} + H_2O \rightarrow [CrO]^{2+} + Ag^+ + 2H^+$

3. $[CrO]^{2+} + Ag^{2+} + H_2O \rightarrow [CrO_2]^+ + Ag^+ + 2H^+$

4. $[CrO_2]^+ + Ag^{2+} + H_2O \rightarrow [CrO_3] + Ag^+ + 2H^+$

5. $2[CrO_3] + H_2O \rightarrow Cr_2O_7^{2-} + 2H^+$

6.



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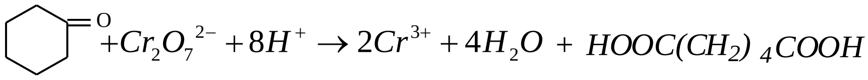

The total equation was：

(1)

3.2 The reaction parameters of the electrode

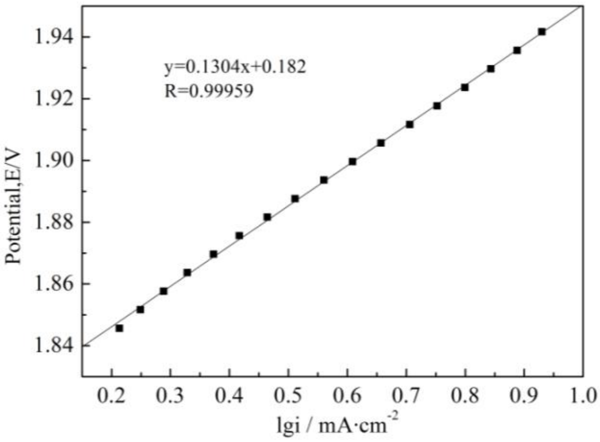

Figure 1. Stable polarization curves of anode

The stable polarization curve of anode is shown in Fig.1. From Fig.1 the anodic Tafel slope can be calculated with the following formula:

$$\frac{d(\Delta\varphi)}{d\lg i}=\frac{2.303RT}{\overset{\leftarrow}{\alpha}F}=0.1304(V) \qquad (2)$$

So the anodic apparent transport coefficient is： $\overset{\leftarrow}{\alpha}=0.47\approx 0.5$

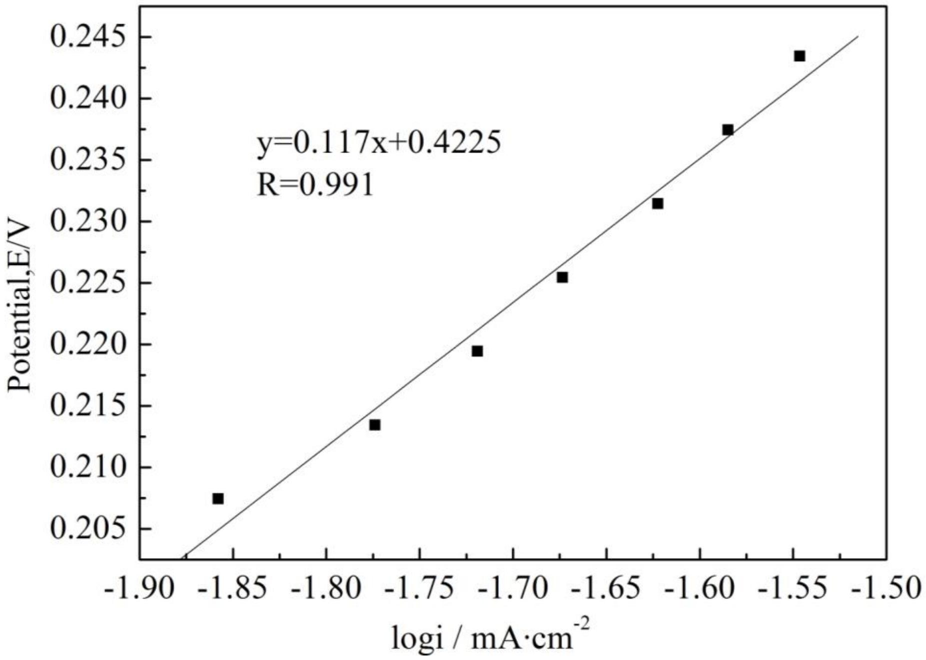

Figure 2. Stable polarization curves of cathode

Similarly, for the cathode, according to the stable polarization curve of cathode from Fig.2, the cathodic Tafel slope was：

$$\frac{d(-\Delta\varphi)}{d\lg i}=\frac{2.303RT}{\vec{a}F}=0.12(V) \qquad (3)$$

And the cathodic apparent transport coefficient is： $\overset{\rightarrow}{\alpha}=0.5$

The stochiometric number of controlled step was calculated by $\overset{\rightarrow}{\alpha}$, $\overset{\leftarrow}{\alpha}$. The oxidation of Cr^{3+} to $Cr_2O_7^{2-}$ needs 6 electrons, and formation of one mol of adipic acid needs eight mol electrons. So the stochiometric number of controlled step should be:

$$v=\frac{8}{\vec{a}+\overset{\leftarrow}{a}}=\frac{8}{0.5+0.5}=8 \qquad (4)$$

The anode electrochemical reaction order of Ag^+ can be obtained according to Fig.3.

$$Z_{Ag^+,C} = (\frac{d\lg i}{d\lg C_{Ag^+}})_{\varphi,pH,T} = 1 \qquad (5)$$

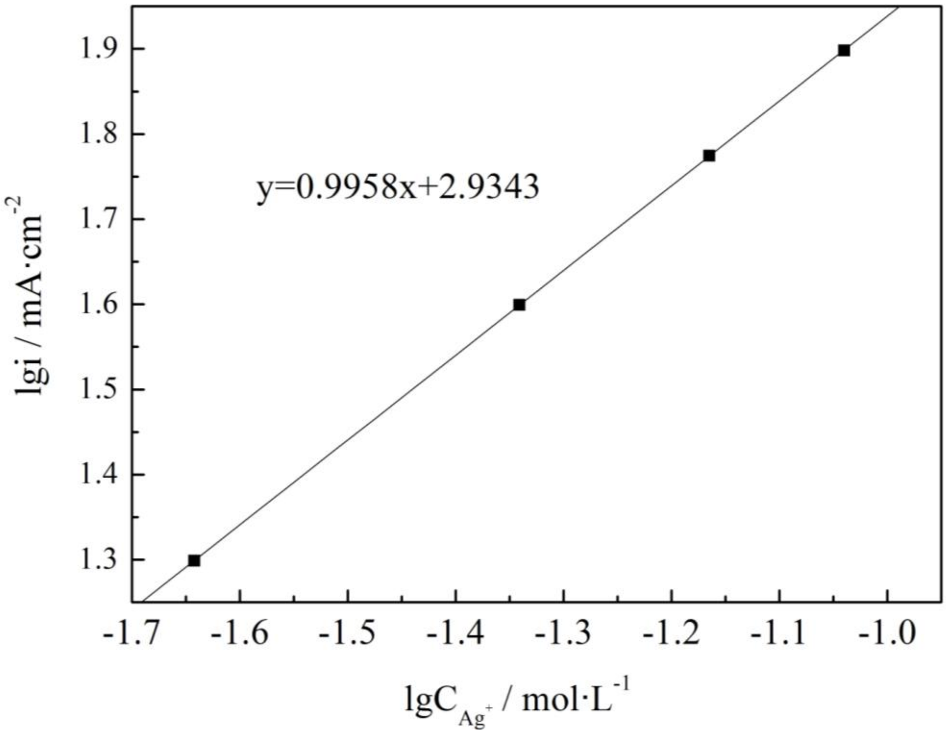

Figure 3. The relationship between lg C_{Ag}+ and lg i

3.3 The derivation of reaction mechanism

The kinetics relationship of electrolysis reaction can be deduced by steady-state approach or quasi-equilibrium state approach under the stable condition. The steady-state approach is not related with the concept of rate determination step and more generally applicable in theory. But if there were only one determination step in multi-step process, the quasi-equilibrium state approach is both convenient and reasonable [13].

Step ① was assumed as the controlled step, the relationship between current density and potential was:

$$i = \overrightarrow{i} - \overleftarrow{i} = 8F\{k_1 C_{Ag^+} \exp(\frac{-\alpha F\varphi}{RT}) - k_{-1} C_{Ag^{2+}} \exp[\frac{(1-\alpha)F\varphi}{RT}]\} \qquad (6)$$

Equation 6 was got by reasoning [13], the final relationship between current density and potential as the following:

$$i=\overrightarrow{i}-\overleftarrow{i}=8F\{k_1C_{Ag^+}\exp(\frac{-\alpha F\varphi}{RT})-K_1(\frac{C_{\text{acid}}}{C_{\text{alcohol}}})^{\frac{1}{8}}C_{Ag^+}C_{H^+}\exp[\frac{(\frac{5}{2}-\alpha)F\varphi}{RT}]\} \quad (7)$$

The electrode potential here is negative enough relative to balance electrode potential. For $\eta \geqslant$ 120/n (mV), the cathodic reaction can be neglected, and the current density of anodic reaction was:

$$i=8Fk_1C_{Ag^+}\exp(\frac{-\alpha F\varphi}{RT}) \quad (8)$$

Put $\Delta\varphi=\varphi-\varphi_{\text{bal ance}}$ into Eq.8, and then $i=8Fk'_1C_{Ag^+}\exp(\frac{-\alpha F\Delta\varphi}{RT})$

When *α*=0.5, *T*=298 K, the cathode reaction Tafel slope was:

$$\frac{d(-\Delta\varphi)}{d\lg i}=\frac{2.303RT}{F}\cdot\frac{1}{\alpha}=\frac{2.303\times 8.314\times 298.2}{96500\times 0.5}=0.12 \quad (9)$$

So $\overleftarrow{\alpha}=0.5$, using the same method, $\overrightarrow{\alpha}=0.5$

According to Eq.4, we can get the stochiometric number of the controlled step.

$$v=\frac{8}{\overrightarrow{a}+\overleftarrow{a}}=\frac{8}{0.5+0.5}=8$$

The electrochemical reaction order of Ag$^+$ was got from Eq.8:

$$Z_{Ag^+,C}=(\frac{d\lg i}{d\lg C_{Ag^+}})_{\varphi,pH,T}=1 \quad (10)$$

As aforesaid, the kinetics equation was derived theoretically from the assumed reaction mechanism. Then the electrochemical reaction order, apparent transfer coefficient, Tafel slope and stochiometric number were calculated from the kinetics equation. The value obtained from the polarization curve agrees well with theoretical value. So the assumed reaction mechanism should be right and we think that the step ① was the control step.

The apparent transfer coefficients of cathode and anode were calculated from $\overrightarrow{\alpha}=\frac{\overrightarrow{\gamma}}{v}+ar$ and $\overleftarrow{\alpha}=\frac{n-\overrightarrow{\gamma}}{v}-\alpha r$, respectively. The values of $\overrightarrow{\gamma}$, *v*, and *r* were got from the assumed mechanism and *a* was assumed as 0.5. The process was:

When step ① was the controlled step, taking v=8， n=8， r=1， $\overrightarrow{\gamma}$ =0（***a***=0.5）

$$\overrightarrow{a}=\frac{\overrightarrow{\gamma}}{v}+\text{a}r=0.5,\quad \overleftarrow{a}=\frac{n-\overrightarrow{\gamma}}{v}-\text{a}r=0.5,\text{so}\,\frac{d(\Delta\varphi)}{d\lg(-i)}=\frac{2.3RT}{0.5F}=0.1182$$

Thus, by taking the first step as the controlled step, the calculated apparent transfer coefficients were consistent with the experimental values. Such a result confirmed in another way that our suggestion on the reaction mechanism was right.

4. CONCLUSION

With reasonable assumption and experimental demonstration, we have come to a conclusion for the electrochemical synthesis of adipic acid in two respects:

First, this electrochemical reaction order for Ag^+ is 1.0. And second, the controlled step is $Ag^+ - e^- \rightarrow Ag^{2+}$.

Such a conclusion highlighted the importance of the oxidation of Ag^+ in the process of electrochemical synthesis of adipic acid. This work may provide some theoretical foundation for industrial production of adipic acid in order to realize a green method in a commercial scale in future.

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