

Kinetics of the Electrocatalytic Oxidation of 2,2-Dimethylolpropionaldehyde

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Abstract A new method of synthesis 2,2-dimethylolpropionic acid from 2,2-dimethylolpropionaldehyde was put forward. The electrochemical oxidation behavior of 2,2-dimethylolpropionaldehyde has been investigated on a Ti/SnO₂ + Sb₂O₄/PbO₂ electrode by cyclic voltammetry (CV) and stable polarization curves in sulfuric acid. The results showed that it was an irreversible reaction controlled by diffusion. The formation mechanism of 2,2-dimethylolpropionic acid in the sulfuric acid was then proposed and the transfer coefficients of the reaction were calculated. It was concluded that $RCHO + QH_{ads} \rightarrow RCHOQH_{ads}$ was the rate-determining step in the electrolysis process. The rate of this step obtained from the assumed process agrees well with experiment.

Keywords 2,2-Dimethylolpropionic acid · 2,2-Dimethylolpropionaldehyde · Electrocatalytic mechanism · Cyclic voltammetry · Kinetics · Rate-determining step

1 Introduction

2,2-Dimethylolpropionic acid is an important organic intermediate in the production of certain pesticides, medicines and dyestuffs [1] and hydrophilic monomers [2, 3]. The chemical oxidation of 2,2-dimethylolpropionaldehyde has been studied by many researchers. For example, 2,2-dimethylolpropionic acid was prepared by the oxidation of 2,2-dimethylolpropionaldehyde with hydrogen peroxide [4, 5]. The process is expensive and the selectivity for the process is poor, and complicated multistep manipulations are required. Because of the presence of two functional groups (aldehyde group and hydroxyl group) in 2,2-dimethylolpropionaldehyde, it is difficult to complete the selective oxidation in a single step of chemical oxidation. This article reports a new method of synthesis 2,2-dimethylolpropionic acid from 2,2-dimethylolpropionaldehyde. The kinetics of the electrocatalytic oxidation of 2,2-dimethylolpropionaldehyde was investigated.

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2 Experimental

2.1 Instruments and reagents

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

2.2 Electrochemical Experiments

2.2.1 Preparation of Anode

The details of the preparation method of the anodes can be found in the literature [6]. A ($7 \times 1 \times 1$) cm titanium plate was used as the support or substrate. Prior to the deposition process, the titanium plate was treated by sandblasting, followed by a chemical treatment in hot 5% (v/v) NaOH solution for 1.0 h. Then the plate was treated in hot 10% (v/v) oxalic acid for 1.0 h. Finally, the support was washed with purified water and dried at 120 °C.

The precursor solution for depositing the $\text{SnO}_2 + \text{Sb}_2\text{O}_4$ coating on the support was a admixture solution, which was prepared from a 10 mL *n*-butyl alcohol solution containing 4 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.332 g SbCl_3 . The precursor solution was quantitatively spread on the pretreated support and the coating was initially treated at 100 °C for 5 min after which, it was annealed at 450 °C for 10 min. This procedure was repeated ten times, and finally the support and coating were annealed 500 °C for 60 min.

The last step was to electroplate PbO_2 on the above substrate in acidic solution. The acidic bath solution for depositing the PbO_2 layer was composed of the following chemicals: $\text{Pb}(\text{NO}_3)_2$: 160.0–170.0 g·L⁻¹, HNO_3 : 3.0–5.0 g·L⁻¹ (pH = 1.0–2.0), and a little $\text{Cu}(\text{NO}_3)_2$.

2.2.2 X-Ray Diffractometer (XRD)

An X-ray diffractometer D/Max-III A (Rigaku Co., Japan), using $\text{CuK}\alpha 1$ ($\lambda = 1.54056 \text{ \AA}$) as the radiation source, was used for identification of the phases.

2.2.3 CV Experiment

In a divided cell, a mesh $\text{Ti}/\text{SnO}_2 + \text{Sb}_2\text{O}_4/\text{PbO}_2$ electrode (1.0×1.0) cm was used as the working electrode, and a Ni counter electrode (1.0×1.0) cm and an SCE (saturated calomel electrode) reference electrode were employed for the experiments. The initial pH was adjusted by addition of either NaOH or H_2SO_4 . The electrolyte volume was 50 mL. All the experiments were carried out at room temperature.

3 Results and Discussion

3.1 X-Ray Diffraction Identification

Since PbO_2 can exist in different phases, X-ray diffraction was used to identify the structure of electrodeposited PbO_2 . A typical XRD pattern of PbO_2 prepared on the $\text{Ti}/\text{SnO}_2 + \text{Sb}_2\text{O}_4$ electrode from a solution containing 0.5 mol·L⁻¹ $\text{Pb}(\text{NO}_3)_2$, at a constant current density of

Fig. 1 A typical XRD pattern of PbO₂

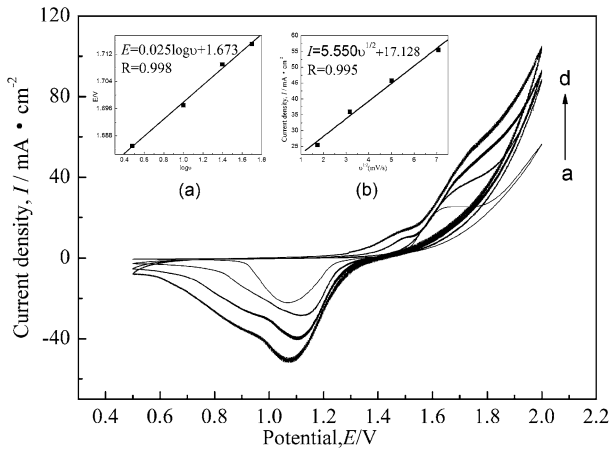
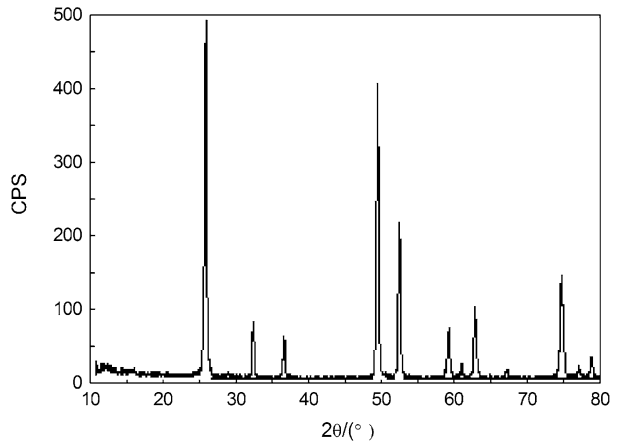


Fig. 2 Cyclic voltammograms at different sweep rates of 3 mV·s⁻¹ (a), 10 mV·s⁻¹ (b), 25 mV·s⁻¹ (c), 50 mV·s⁻¹ (d)

20 mA·cm⁻² for 30 min is shown in Fig. 1. The β-PbO₂ may be identified from its intense lines (25.8 °2θ), (32.45 °2θ) and (49.85 °2θ). According to previously reported work, the lead dioxide electrodeposited from acidic Pb(NO₃)₂ solution exists in the β-PbO₂ form, but from alkaline solution, α-PbO₂ is the major form [7, 8]. As shown in Fig. 1, most of the characteristic peaks of β-PbO₂ have been observed for the deposited sample.

3.2 Effect of Sweep Rates

The influence of the scan rate on the cyclic voltammetry behavior of the Ti/SnO₂+Sb₂O₄/PbO₂ electrode in 0.05 mol·L⁻¹ H₂SO₄ + 0.10 mol·L⁻¹ 2,2-dimethylpropionaldehyde is shown in Fig. 2. As the scan rate increases, the anodic peak potentials shift to more positive values and the cathodic peak potentials are shifted in a slightly positive direction. It is also observed from Fig. 2 that as the scan rate increases, the current densities increase in the forward sweep and the current densities of the cathodic peak increase in the reverse sweep. The plot of the CV peak currents *I*_{pa} against the square root of the voltage scan rate,

$v^{1/2}$, gives a reasonable linear relationship, $R = 0.998$ (inset (a) in Fig. 2). In semi-infinite diffusion-controlled cyclic voltammetry for liquid electrolytes, I_{pa} against $v^{1/2}$ gives a linear relationship regardless of scan rate for a kinetically uncomplicated redox reaction. In this study, the linear relationship between I_{pa} and $v^{1/2}$ demonstrates that the electrochemical formation reaction is a diffusion-controlled process. Additionally, it is also found that the peak potential, E_p , shows a linear variation with the logarithm of the scan rate ($R = 0.995$) as indicated in inset (b) of Fig. 2. These findings suggest that the anodic processes, in the 2,2-dimethylpropionaldehyde oxidation potential range, are under diffusion control, and the corresponding system is irreversible.

3.3 Effect of the 2,2-Dimethylpropionaldehyde Concentration

In order to further clarify the electrochemical oxidation mechanism of 2,2-dimethylpropionaldehyde on the $\text{Ti/SnO}_2 + \text{Sb}_2\text{O}_4/\text{PbO}_2$ electrode, the effect of 2,2-dimethylpropionaldehyde concentration on CV responses was investigated. It is shown from Fig. 3 that the anodic peak is not in evidence whereas the anodic current increases markedly after adding $0.5 \text{ mol}\cdot\text{L}^{-1}$ 2,2-dimethylpropionaldehyde, so that 2,2-dimethylpropionaldehyde may take part in the reaction. The anode reactions mainly include the oxidation of 2,2-dimethylpropionaldehyde with oxygen evolution. It is observed from Fig. 4 that as the

Fig. 3 Cyclic voltammograms in the absence and presence of $0.05 \text{ mol}\cdot\text{L}^{-1}$ 2,2-dimethylpropionaldehyde

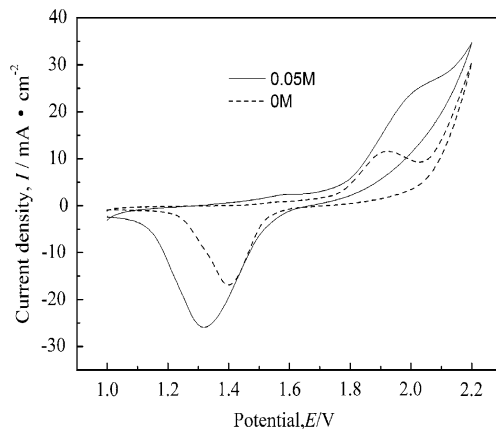


Fig. 4 Cyclic voltammograms of 2,2-dimethylpropionaldehyde with concentration $0.025 \text{ mol}\cdot\text{L}^{-1}$ (a), $0.05 \text{ mol}\cdot\text{L}^{-1}$ (b), $0.075 \text{ mol}\cdot\text{L}^{-1}$ (c) and $0.10 \text{ mol}\cdot\text{L}^{-1}$ (d); $\nu = 3 \text{ mV}\cdot\text{s}^{-1}$

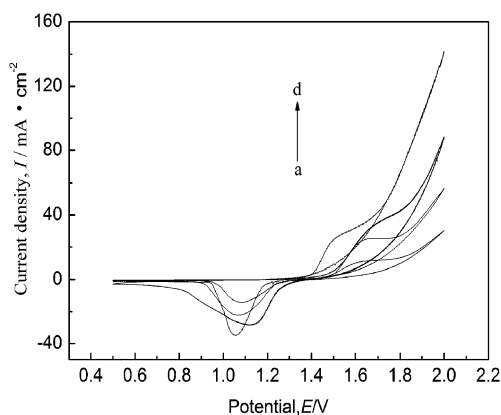
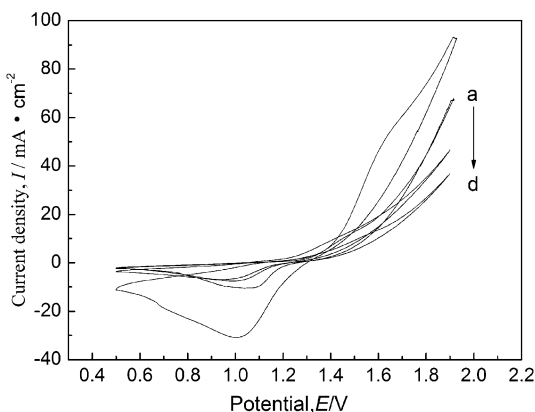


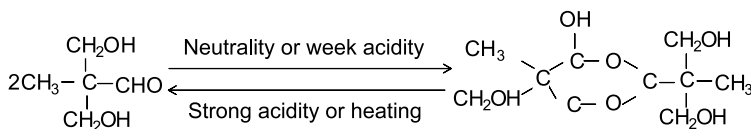
Fig. 5 Cyclic voltammograms of 0.1 mol·L⁻¹ 2,2-dimethylolpropionaldehyde at pH = 1 (a), 2 (b), 3 (c) and 5 (d), respectively



2,2-dimethylolpropionaldehyde concentration increases, the current densities increase in the forward sweep and the current densities of the cathodic peak increase in the reverse sweep. This indicates that the oxidation reaction of 2,2-dimethylolpropionaldehyde contributes to the anodic current and leads to an increase in the total anodic current [9]. The initial potential of oxidation is 1.40 V when 2,2-dimethylolpropionaldehyde was present with a concentration higher than 0.10 mol·L⁻¹, whereas as the concentration decreases, the anodic peak potentials shift to less negative values and the cathodic peak potentials are shifted in a slightly negative direction, except for curve c, which is probably because O₂ evolution begins to occur; the higher the concentration of 2,2-dimethylolpropionaldehyde, the more significant is the O₂ evolution reaction which is otherwise limited by diffusion of 2,2-dimethylolpropionaldehyde to the electrode. Therefore, high concentrations of 2,2-dimethylolpropionaldehyde are propitious to the electrooxidation reaction.

3.4 Effect of the H₂SO₄ Initial Concentration

The stability of the acid-proof electrode and the form of the reactant are important in the electrolysis process. Figure 5 shows the cyclic voltammograms of 0.10 mol·L⁻¹ 2,2-dimethylolpropionaldehyde with different initial concentrations of sulfuric acid. With increasing concentration of sulfuric acid, the current density obviously increases at the same anode potential when the potential is above 1.50 V. The current density at pH = 3 is almost as high as that at pH = 5. The current densities increase with decreasing pH when the pH is lower than 3. An aqueous solution of a high concentration of sulfuric acid can maintain the stability of β-PbO₂ [10] and improve its electrocatalytic activity. When pH > 3, 2,2-dimethylolpropionaldehyde mainly exists in a polymeric form [11]. At the same time, there is an equilibrium between the monomer and the polymer of 2,2-dimethylolpropionaldehyde in weakly acidic and neutral solutions, which is expressed as follows: the polymer can be converted into the monomer by heating or by increasing acidity.



The aldehyde group in the polymer is enshrouded because the aldehyde group is lactonized in the weakly acidic and neutral media. So the electrolysis process must occur in

Table 1 The relationship of current density and potential on the anode

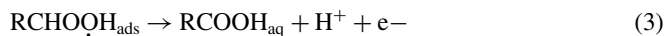
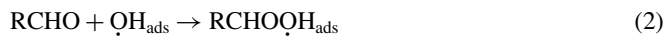
Current density, i (mA·cm ⁻²)	3.92211	4.97096	6.30028	7.98509	10.12022
Potential, E (V)	1.7003	1.70055	1.7117	1.7201	1.7242
Current density, i (mA·cm ⁻²)	12.82655	16.25661	20.60345	26.11319	33.09634
Potential, E (V)	1.73046	1.73869	1.74292	1.75115	1.75538

strongly acidic solution in order to keep the electrode stable and to ensure the reactant exists in the monomeric form.

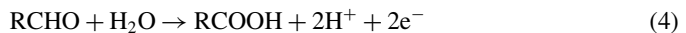
3.5 The Electrocatalytic Mechanism of 2,2-Dimethylolpropionaldehyde

3.5.1 The Assumed Mechanism

The electrocatalytic mechanism of 2,2-dimethylolpropionaldehyde was assumed as [12–14]:



The total equation is:



where R represents: CH₃C(CH₂OH)₂; OH represents: QH_{ads}; RCHOH represents: RCHOQH_{ads}, and RCOOH represents: RCOOH_{aq}.

3.5.2 The Response Parameter of the Electrolysis

In a divided cell, a mesh Ti/SnO₂ + Sb₂O₄/PbO₂ electrode (1.0 × 1.0) cm was used as the working electrode, and a Ni counter electrode (1.0 × 1.0) cm and an SCE reference were employed for the CV experiment. Some data are presented in Table 1.

According to the stable polarization curve of the anode in Fig. 6 (Table 1), the anodic Tafel rate of slope was:

$$\frac{d(\Delta\varphi)}{d\log_{10}i} = \frac{2.303RT}{\vec{\alpha}F} = 0.06(\text{V}) \quad (5)$$

So the anodic apparent transport coefficient is: $\vec{\alpha} = 1$.

According to the stable polarization curve of cathode in Fig. 7 (Table 2), the cathodic Tafel rate of slope is:

$$\frac{d(-\Delta\varphi)}{d\log_{10}i} = \frac{2.303RT}{\overleftarrow{\alpha}F} = 0.06(\text{V}). \quad (6)$$

So the anodic apparent transport coefficient is: $\vec{\alpha} = 1$.

The experimental data of the rate-controlling step was obtained from $\vec{\alpha} - \overleftarrow{\alpha}$ and the oxidation of 2,2-dimethylolpropionaldehyde to 2,2-dimethylolpropionic acid that released two electrons.

$$v = \frac{2}{\vec{\alpha} + \overleftarrow{\alpha}} = \frac{2}{1 + 1} = 1. \quad (7)$$

Fig. 6 Stable polarization curves of the anode

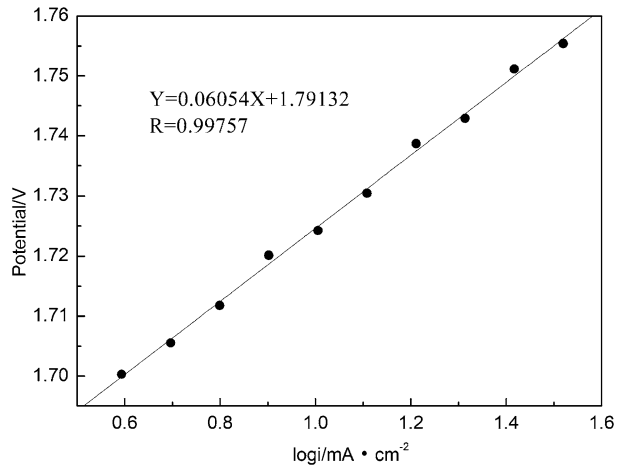
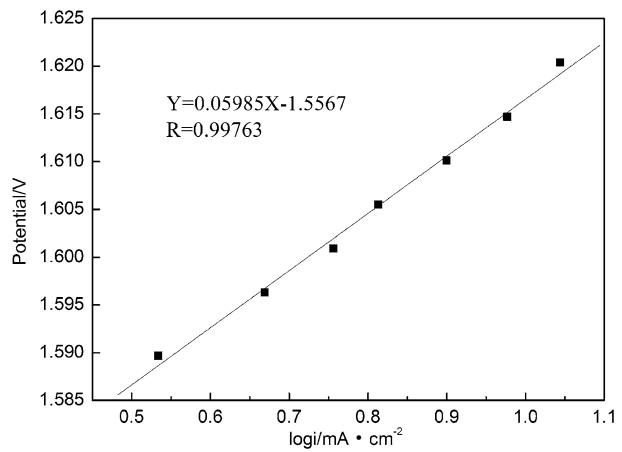


Table 2 The relationship of current density and potential on the cathode

Current density, i (mA·cm ⁻²)	11.05936	9.48047	7.94182	6.50145
Potential, E (V)	1.6204	1.6147	1.6101	1.6055
Current density, i (mA·cm ⁻²)	5.70311	4.66874	3.41829	
Potential, E (V)	1.6009	1.5963	1.5897	

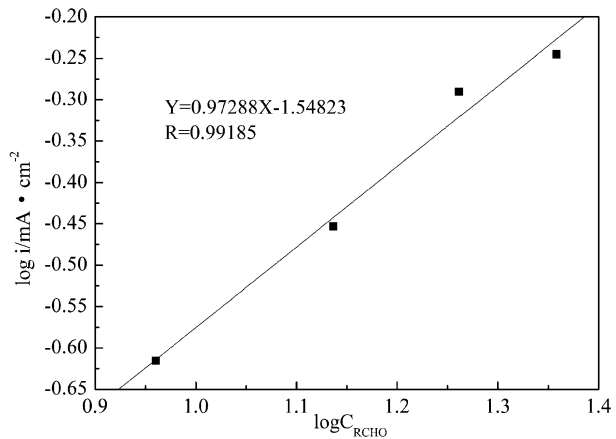
Fig. 7 Stable polarization curves of the cathode



The cathodic electrochemical reaction order of 2,2-dimethylpropionaldehyde was obtained from the stable polarization curve according to Fig. 8.

$$Z_{\text{RCHO,C}} = \left(\frac{d \log_{10} i}{d \log_{10} C_{\text{RCHO}}} \right)_{\varphi, C_{\text{H}^+}, T} = 0.97288 \approx 1.0. \quad (8)$$

Fig. 8 The relationship between $\log_{10}C_{\text{RCHO}}$ and $\log_{10}i$



3.5.3 The Derivation of Electrocatalytic Mechanism

The kinetic relationship of electrode reaction can be deduced by a steady-state method or quasi-equilibrium state method in the stable condition. Moreover, the steady-state method is not related to the concept of the rate-determining step. However, if there were only one rate-determining step in a multi-step process, the quasi-equilibrium state method is convenient [15].

The first step was assumed as the rate-controlling step and the relationship between the current density and potential was:

$$i = \vec{i} - \overleftarrow{i} = 2F \left\{ k_1 \exp\left(\frac{-\alpha F \varphi}{RT}\right) - k_{-1} C_{\text{HO}} C_{\text{H}^+} \exp\left(\frac{(1-\alpha) F \varphi}{RT}\right) \right\}. \quad (9)$$

When the first was assumed as the rate-controlling step, others were in a balanced state, so according to the quasi-equilibrium state method, the relationship between current density and potential finally is:

$$i = \vec{i} - \overleftarrow{i} = 2F \left\{ k_1 \exp\left(\frac{-\alpha F \varphi}{RT}\right) - k_{-1} \frac{k_{-2} k_{-3}}{k_2 k_3} C_{\text{RCHO}}^{-1} C_{\text{RCOOH}} C_{\text{H}^+}^2 \exp\left(\frac{(3-\alpha) F \varphi}{RT}\right) \right\}. \quad (10)$$

If $K = \frac{k_{-2} k_{-3}}{k_2 k_3}$, then Eq. 10 as becomes:

$$i = \vec{i} - \overleftarrow{i} = 2F \left\{ k_1 \exp\left(\frac{-\alpha F \varphi}{RT}\right) - k_{-1} K C_{\text{RCHO}}^{-1} C_{\text{RCOOH}} C_{\text{H}^+}^2 \exp\left(\frac{(3-\alpha) F \varphi}{RT}\right) \right\}. \quad (11)$$

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

$$i = \vec{i} - \overleftarrow{i} = 2F k_1 \exp\left(\frac{-\alpha F \varphi}{RT}\right). \quad (12)$$

We can derive the electrochemical reaction order of RCHO as 0 from Eq. 12, whereas the order was one from the experimental data. Obviously, the theoretical value does not agree with the experimental value. Therefore, the first step was not the rate-controlling step.

If step 2 was assumed to be the rate-controlling step and the relationship between current density and potential is:

$$i = \vec{i} - \overleftarrow{i} = 2F \left\{ k_2 C_{\text{RCHO}} C_{\text{OH}} \exp\left(\frac{-\alpha F\varphi}{RT}\right) - k_{-2} C_{\text{RCHOOH}} \exp\left(\frac{(1-\alpha)F\varphi}{RT}\right) \right\}. \quad (13)$$

When the second step was assumed to be the rate-controlling step, using the same method will give:

$$i = \vec{i} - \overleftarrow{i} = 2F \left\{ k_2 \frac{k_1}{k_{-1}} C_{\text{RCHO}} C_{\text{H}^+}^{-1} \exp\left(\frac{-(1+\alpha)F\varphi}{RT}\right) - k_{-2} \frac{k_{-3}}{k_3} C_{\text{RCOOH}}^{-1} C_{\text{H}^+}^{-1} \exp\left(\frac{(2-\alpha)F\varphi}{RT}\right) \right\}. \quad (14)$$

If $K_2 = \frac{k_2 k_1}{k_{-1}}$, $K_3 = \frac{k_{-2} k_{-3}}{k_3}$, then Eq. 14 is as follows:

$$i = \vec{i} - \overleftarrow{i} = 2F \left\{ K_1 C_{\text{RCHO}} C_{\text{H}^+}^{-1} \exp\left(\frac{-(1+\alpha)F\varphi}{RT}\right) - K_2 C_{\text{RCOOH}}^{-1} C_{\text{H}^+}^{-1} \exp\left(\frac{(2-\alpha)F\varphi}{RT}\right) \right\}. \quad (15)$$

The electrochemical reaction order of RCHO was counted for according to Eq. 15

$$Z_{\text{RCHO,C}} = \left(\frac{d \log_{10} i}{d \log_{10} C_{\text{RCHO}}} \right)_{\varphi, T, C_{\text{H}^+}} = 1.0. \quad (16)$$

A kinetic equation was derived from the assumed reaction mechanism. Then the electrochemical reaction order was calculated from the kinetics equation. The value obtained from the polarization curve agrees well with theoretical value according to Eq. 15. Thus the assumed reaction mechanism is correct and the second step is the rate-controlling step. The result is consistent with the research findings from the cyclic voltammograms.

3.5.4 Demonstration of the Rate-Controlling Step

The apparent transfer coefficients of cathode and anode were calculated from $\vec{\alpha} = \frac{\vec{\gamma}}{\nu} + ar$ and $\overleftarrow{\alpha} = \frac{n-\vec{\gamma}}{\nu} - ar$, respectively. The values of $\vec{\gamma}$, ν and r were obtained from the assumed mechanism. The calculated process was:

When the first step is the rate-controlling step: $\vec{\gamma} = 0, \nu = 1, r = 1 (a = 0.5)$

Therefore, $\vec{\alpha}_1 = 0.5$ and $\overleftarrow{\alpha}_1 = 1.5$.

When the second step is the rate-controlling step, $\vec{\gamma} = 1, \nu = 1, r = 0 (a = 0.5)$

Therefore, $\vec{\alpha}_1 = 1, \overleftarrow{\alpha}_1 = 1$.

We can see that when the second step is taken as the rate-controlling step, the calculated apparent transfer coefficient is consistent with the experimental value. Therefore, the assumed reaction mechanism is correct.

4 Conclusions

In conclusion, this work initiated an interesting research path by showing that the electrolysis of 2,2-dimethylolpropionaldehyde in sulfuric acid can lead to the formation of 2,2-dimethylolpropionic acid by a mechanism involving two electrons per molecule of reactant.

The electrochemical oxidation reaction was shown to be a diffusion-controlled process, and the corresponding system was reversible. From the assumed electrochemical oxidation mechanism, we know that the assumed reaction mechanism was correct and the rate-controlling step was $\text{RCHO} + \text{QH}_{\text{ads}} \rightarrow \text{RCHOQH}_{\text{ads}}$. This mechanism is in good agreement with the experimental observations.

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