Electrochemical Behavior of Electrocatalytic Synthesis of Oxalic Acid from Acetylene at Pt Electrode

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Abstract:

Electrocatalytic synthesis of oxalic acid from acetylene has been achieved at Pt electrode. The electrocatalytically synthesized oxalic acid has been characterized by FTIR (Fourier transform infrared spectroscopy) and UV-Vis (UV-Vis spectrophotometry). Influence of electrode material, Na_2SO_4 concentration, acetone volume fraction, temperature and scan rate have been investigated by CV (cyclic voltammetry). The analysis results show that oxalic acid has been successfully electrocatalytically synthesized from acetylene at the very stable Pt electrode under ambient temperature and pressure, the supporting electrolyte is Na_2SO_4 (0.5 M) with acetone (2% by volume), the reaction time is 8 h and the conversion efficiency is larger than 20%. The E_a (apparent activation energy) of electrocatalytic oxidation reaction of acetylene at the Pt electrode is 14.42 $kJ\cdot mol^{-1}$, the electrocatalytic oxidation process of acetylene is irreversible and under adsorption control. In addition, the reaction mechanism of the electrocatalytic oxidation process of acetylene to oxalic acid has been envisaged successfully based on the principle of adsorption and desorption at Pt electrode surface. It exhibits the excellent electrocatalytic performance of Pt in the electrocatalytic oxidation process of acetylene and heralds more broad potential application prospect of acetylene in chemical industry field.

Keywords: electrocatalytic synthesis; oxalic acid; acetylene; cyclic voltammetry

Introduction

Comprehensive comparison of existing synthesis technologies of oxalic acid (1-3) shows that some of them need higher temperature and higher pressure, higher requirements for production equipment; some processes are more complex; some are backward in technology or need higher standard raw materials; some lead to higher energy consumption and more serious pollution; some sources of raw materials are too difficult to obtain. So it is particularly urgent to seek a green synthetic route of clean, efficient and energy saving. In 1919, it was found that oxalic acid could be prepared on a practical scale, in almost pure condition, from acetylene and HNO_3, with $Hg(NO_3)_2$ as the catalyst (4). At the same time, as a kind of green synthesis method, electrochemical synthesis has been favored widely (5). So production of oxalic acid from a cheap carbon source by electrochemical synthesis appears more attractive as an eco-friendly, non-hazardous process yielding oxalic acid at lower cost.

This study puts forward a kind of view to electrocatalytic synthesis of oxalic acid from acetylene at Pt electrode. The electrochemical behavior of electrocatalytic synthesis of oxalic acid from acetylene in Na_2SO_4 has been examined by CV. In addition, the reaction mechanism of the electrocatalytic oxidation process of acetylene to oxalic acid has been envisaged successfully based on the principle of adsorption and desorption. It can effectively solve obvious deficiency among the existing production processes of oxalic acid (6-8). The schematic diagram of reaction mechanism of electrocatalytic oxidation of acetylene to oxalic acid is shown in Figure 1.

Experimental

Instruments and Reagents

All chemical reagents and solvents in present work were of analytical grade and used as received without further purification. All aqueous solutions for all experiments were prepared using doubly deionized water. Pt, Ni, Pd and SCE (saturated calomel electrode) electrodes were purchased from Gaoss Union Technology Co. Ltd., Wuhan, China. Ti based oxides electrode and Ti based Cu-Ag alloys electrode were self-made in the laboratory according to literature procedure (9, 10). A direct current regulated power supply (HB17301SC, Hongbao Electric Group Co.

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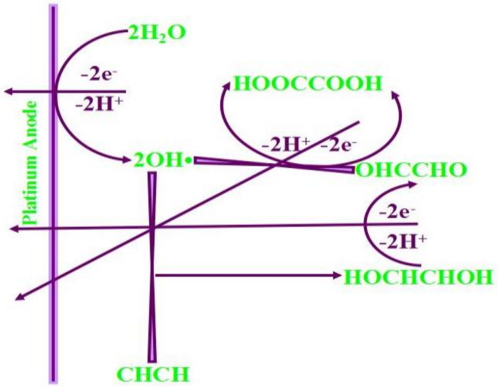

Figure 1. The schematic diagram of electrocatalytic oxidation of acetylene to oxalic acid at Pt electrode.

Ltd., China) was used to the process of electrocatalytic synthesis of oxalic acid. A FTIR spectrometer (FTIR-8400S, Shimadzu Corporation, Japan) and an UV-Vis spectrophotometer (Cary50, Varian Corporation, The United States) were used to characterize electrocatalytically synthesized oxalic acid. A CHI660D potentiostatic electrochemical station (Shanghai Chenhua Instruments Corporation, China) was used to measure the CVs. All the experiments were performed at ambient temperature and pressure except these clearly marked.

Electrochemical Experiment

Electrochemical experiments were performed in a three-electrode cell: Pt, Ni, Ti based oxides and Ti based Cu-Ag alloys electrode, working electrode; Pd, counter electrode; SCE, reference electrode (11-13). All the experiments were carried out in Na_2SO_4 (0.1~1.0 M, 100 mL). Acetylene (20 mL·min^{-1}) must be piped into the solution of Na_2SO_4 for 10 min before carrying out the experiments.

Electrocatalytic Synthesis of Oxalic Acid (6, 7, 11, 12)

Electrocatalytic synthesis of oxalic acid was performed in a devided cell, a Pt electrode (0.6 cm^2) and a Pd electrode (1.9 cm^2) were used as anode and cathode respectively for the experiment. All the experiments were carried out in Na_2SO_4 (0.5 M) with acetone (2% by volume) as the anolyte (100 mL) and H_2SO_4 (1.0 M) as the catholyte (100 mL) respectively. The current density was 16.67 mA·cm^{-2}. Acetylene (20 mL·min^{-1}) must be piped into the anolyte for 10 min before carrying out the experiments.

Results and Discussion

Electrochemical Behavior of Acetylene

Influence of Electrode

The CV of acetylene in 1.0 M Na_2SO_4 at Pt, Ni, Ti based oxides and Ti based Cu-Ag alloys electrodes was investigated. As shown in Figure 2(a), in the presence of acetylene, an anodic peak begins to appear at about 0.30 V, the i_{pa} (anodic peak current) reaches to the maximum at about 0.98 V. But it is not in evidence without added acetylene, so it can be concluded that acetylene takes part in the reaction and be in-site oxidized by OH· (hydroxyl radical) from the electrolysis process of Na_2SO_4 solution. Pt shows a well-defined oxidation peak approximately, whereas at all other electrodes in the process is overshadowed by the anodic limit as shown in Figure 2(b), 2(c) and 2(d). That is to say Pt shows good electrocatalytic effect in the process of electrocatalytic oxidation of acetylene. From the practical point of view, the electrocatalytic activity allows one not only to reduce the energy consumption, but also, and more importantly, to enhance the current efficiency (14).

The stability of the Pt electrode was also examined by performing cyclic voltammograms of 15 repetitive cycles at scan rate of 50 mV·s^{-1} in 1.0 M Na_2SO_4 saturated with acetylene. As shown in Figure 3, there are only slight changes in the i_p (peak current) and the E_p (peak potential). Thus the stability of the Pt electrode used for electrocatalytic studies was established.

Influence of Na_2SO_4 Concentration

It is observed from Fig. 4 that an anodic peak appears at about 0.98 V showing that acetylene has been in-site electrocatalytically oxidized. It is logically true that higher the Na_2SO_4 concentration, higher the ionic strength and lower the electrical resistance. When it comes to each curve, there is an obvious increase in the i_{pa}s at the beginning which is due to the increased Na_2SO_4 concentration. Afterwards the i_{pa}s decrease, indicating that excessive ionic strength is not conducive to the electrocatalytic oxidation process of acetylene at Pt electrode because of salt effect. The inset shows that 0.5 M Na_2SO_4 is appropriate due to the maximum i_{pa} and acetylene have been oxidized significantly in it at the Pt electrode.

Influence of Acetone Volume Fraction

Figure 5 shows that acetylene has been electrocatalytically oxidized at about 0.98 V. Notably, acetone increases its solubility (15) resulting in different i_{pa}s from different volume fraction of acetone of 0%, 1%, 2%, 4% 5% and 10% in electrolyte. Acetone (2% by volume) has been chosen to be added in to 0.5 M Na_2SO_4 because it gives the highest i_{pa} as shown in Figure 5(d).

Influence of Temperature

Influence of temperature variation on electrocatalytic oxidation of acetylene at Pt electrode was

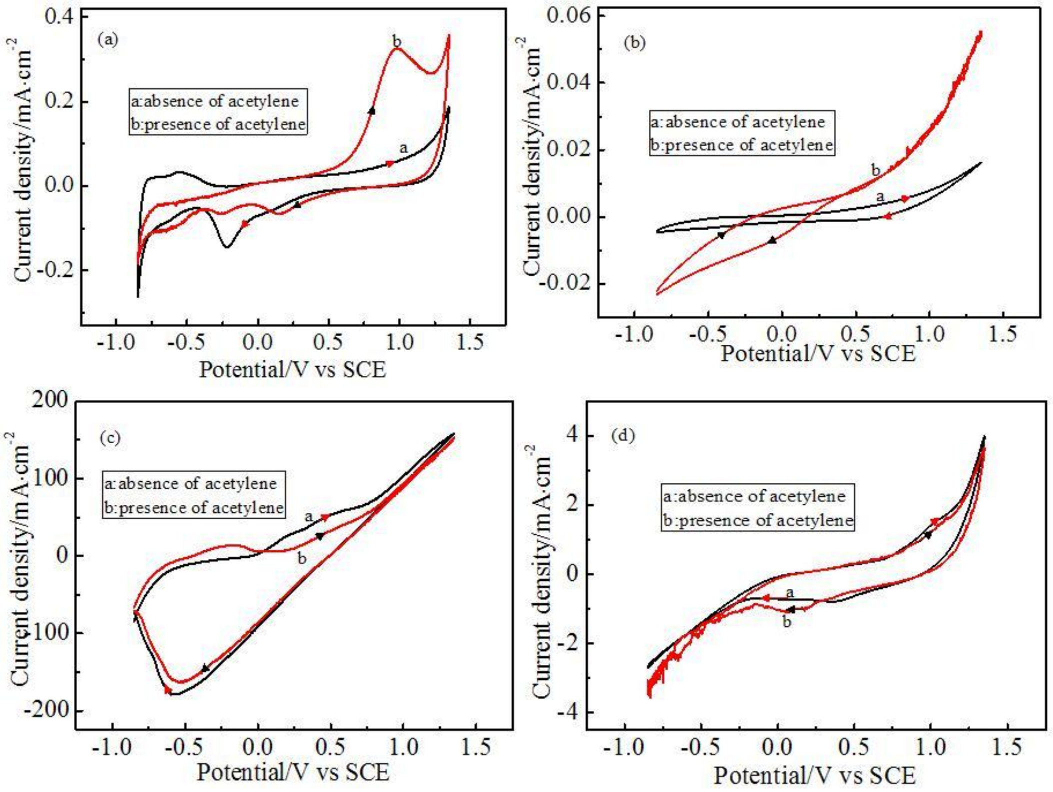

Figure 2. CVs of acetylene recorded at v = 50 mV·s^{-1} in 1.0 M Na_2SO_4 at different electrodes of (a)Pt, (b)Ni, (c)Ti based oxides and (d)Ti based Cu-Ag alloys electrodes.

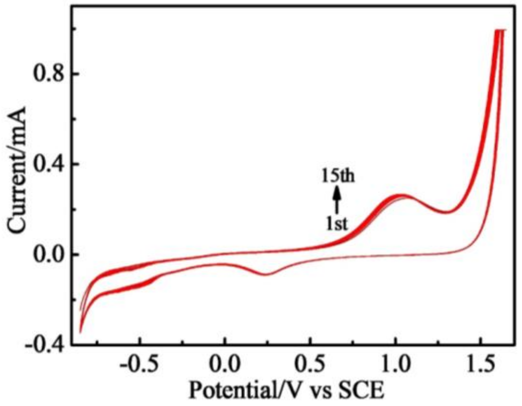

Figure 3. CVs of acetylene recorded in 1.0 M Na_2SO_4 at Pt electrode. Curves correspond to the 1st to the 15th potential scans at v = 50 mV·s^{-1} .

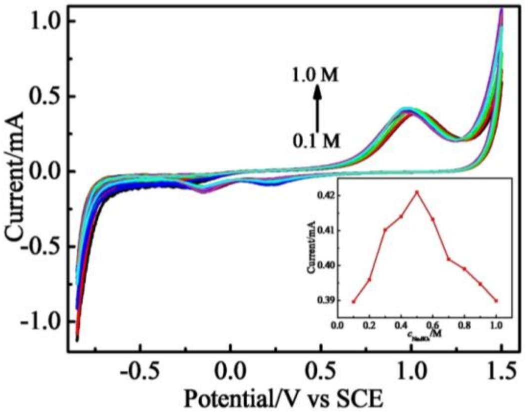

Figure 4. CVs of acetylene recorded at v = 50 mV·s^{-1} in different concentration Na_2SO_4 of 0.1~1.0 M at Pt electrode.

investigated by CV at different temperatures of 293, 303, 313, 323 and 333 K in 0.5 M Na_2SO_4 with acetone (2% by volume). It can be seen from Figure 6 that the shape remains unchanged at different temperatures. It is reasonable that higher the temperature, higher the i_{pa} and more negative the E_p will be. However, the inset shows a severe increase in the i_{pa}s at the beginning, which is due to increased number of activated molecules because of increased temperature resulting in faster reaction rate. Afterwards the i_{pa}s vary gently, indicating gentle variation of reaction rates. This is because the solubility of acetylene in 0.5 M Na_2SO_4 with acetone (2% by volume) decreases due to extremely high temperature and the boiling point of acetone being 329 K as listed in literature (16).

Polarization Curves at Different Temperature

Polarization curves of Pt electrode in 0.5 M Na_2SO_4 with acetone (2% by volume) in the presence of saturated acetylene at a fixed scan rate of 5 mV·s^{-1} at 293, 303, 313, 323 and 333 K are shown in

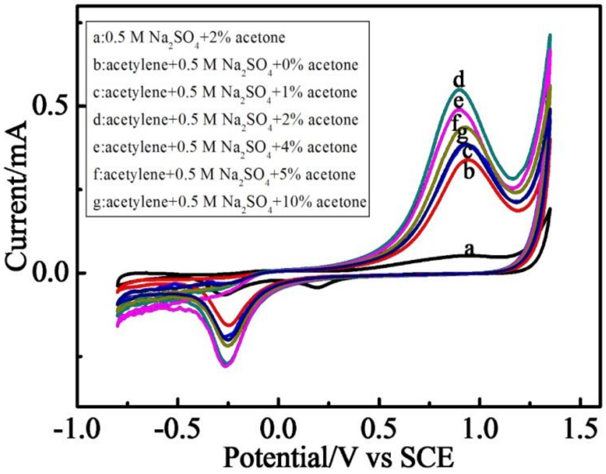

Figure 5. CVs of acetylene recorded at v = 50 mV·s^{-1} in 0.5 M Na_2SO_4 with acetone (0%, 1%, 2%, 4%, 5% and 10% by volume) at Pt electrode.

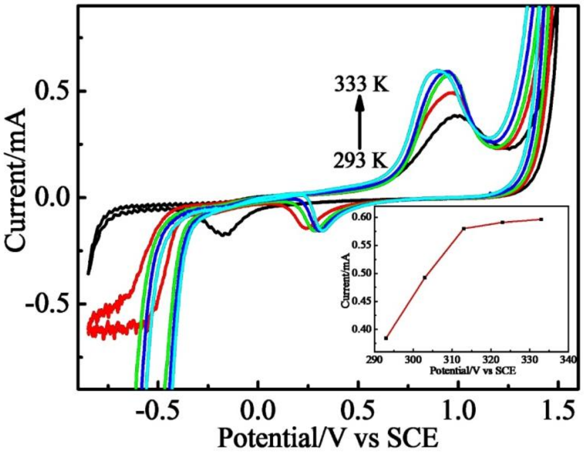

Figure 6. CVs of acetylene recorded at v = 50 mV·s^{-1} in 0.5 M Na_2SO_4 with acetone (2% by volume) at Pt electrode at different temperatures of 293-333 K.

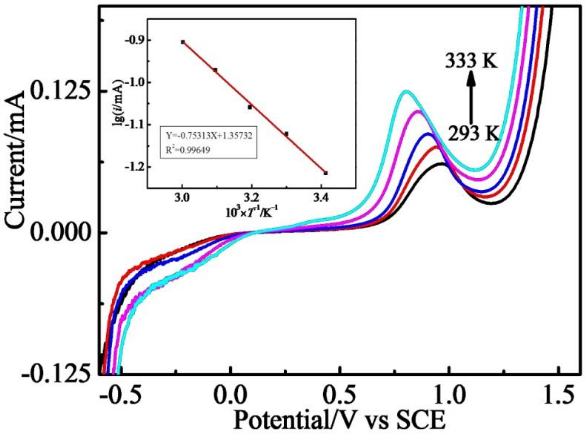

Figure 7. Polarization curves in 0.5 M Na_2SO_4 with acetone (2% by volume) at Pt electrode at different temperatures of 293~333 K at v =5 mV·s^{-1}. The inset shows plots of the lg$i$ versus T^{-1}.

Figure 7. The inset shows the relationship of lg$i$ and T^{-1}. The corresponding linear equation is as

$$\lg i = 1.35732 - 0.75313 \times \frac{1}{T},\ R^2 = 0.99649.$$

According to Arrhenius equation as $\lg i = a - \frac{E_a}{2.303RT}$, the E_a of electroctalytic oxidation reaction of acetylene at Pt electrode can be calculated as 14.42 kJ·mol^{-1}.

In the above equation, i is current, T is temperature, a is a constant, R is the Molar gas constant (8.314 J·mol^{-1}·K^{-1}), E_a is the reaction apparent activation energy.

Influence of Scan Rate

Figure 8 shows the CV corresponding to the response of acetylene at Pt electrode in 0.5 M Na_2SO_4 with acetone (2% by volume) at scan rates of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 150, 180, 200, 220, 250, 280 and 300 mV·s^{-1}. As the scan rate increases, the E_{pa}s (anodic peak potential) shift to more positive values (from 0.956 V to 1.088 V) and the i_{pa}s increase in the forward sweep (from 8.121×10^{-2} mA to 1.326 mA), indicating the occurrence of irreversibility of the electron transfer process (17-19). The inset shows that the i_{pa}s are linearly dependent on the scan rate in the range of 10~300 mV·s^{-1}, R^2=0.99294, implying the electrochemical characteristic of the surface-confined redox reactant rather than the freely diffusing species meaning the anodic process, in the acetylene oxidation potential range, are under adsorption control (20).

Influence of Reaction Time

FTIR spectras of influence of reaction time on electrocatalytic oxidation process of acetylene are shown in Figure 9. It shows that different reaction time leads to different electrolysate. The band at 1068 cm^{-1} and 1210 cm^{-1} are assigned to C-C and C-O stretching. The absorption peak at 1713 cm^{-1} may be due to -COO in the carboxylic acid. The bond of -OH and association effect on the bond of -OH in carboxylic acid lead to the stronger absorption peak at 3470 cm^{-1} (21).

It can be deduced that the characteristic absorption peak of -OH dominates when the reaction time is within 3.5 h, and the concentration of -OH in the electrocatalytic system shows a trend of decrease followed by increase. It suggests that the electrolysis of Na_2SO_4 solution plays a major role during the initial period of reaction. When the reaction time is more than 3.5 h, more oxalic acid is electrocatalytically synthesized, hence the characteristic absorption peaks

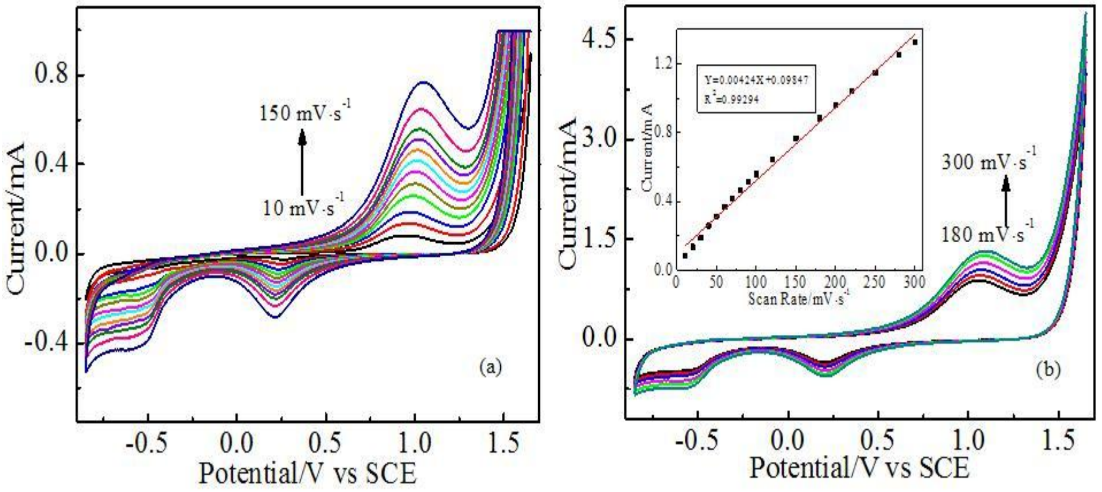

Figure 8. CVs of acetylene recorded in 0.5 M Na_2SO_4 with acetone (2% by volume) at Pt electrode at different scan rates of 10~300 mV·s^{-1}. The inset shows plots of the i_{pa} versus scan rate.

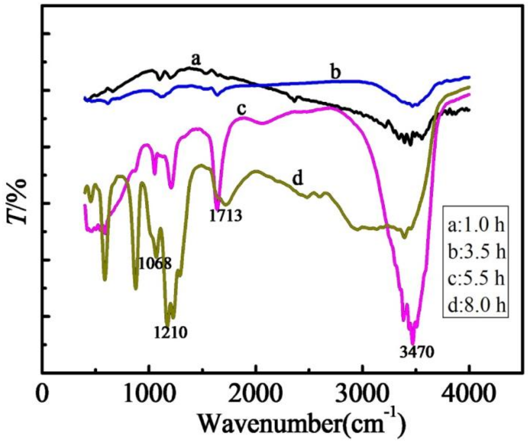

Figure 9. FTIR spectra of influence of reaction time on the electrocatalytic oxidation process of acetylene.

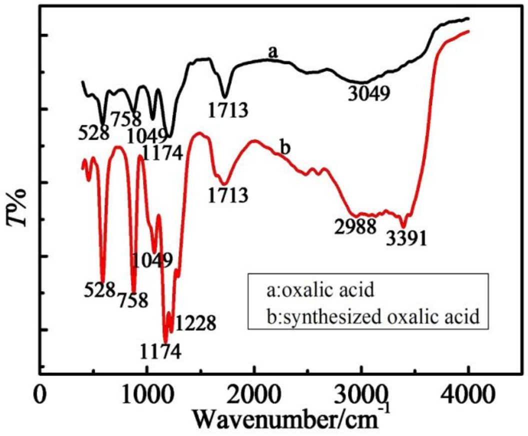

Figure 10. FTIR spectras of pure and electrocatalytically synthesized oxalic acid.

of all functional groups belong to oxalic acid are gradually stronger; just the opposite, the characteristic absorption peak of group belong to -OH is gradually weaker. When the reaction time reaches to 8 h, the characteristic absorption peaks of all functional groups belong to oxalic acid and -OH begins to be weaker again. It shows that electrocatalytically synthesized oxalic acid may be further oxidized because of the extension of reaction time. This observation reveals as that the best reaction time should be controlled to be 8 h.

Characterization of Electrocatalytically Synthesized Oxalic Acid

FTIR Spectra Analysis

The FTIR spectra of pure and electrocatalytically synthesized oxalic acid are shown in Figure 10. Electrocatalytically synthesized oxalic acid displays very similar spectra, implying the similar structures of pure oxalic acid. The bands at 528 and 758 cm^{-1} are likely to correspond to the electrolyte Na_2SO_4 solution. The bands at 1049, 1174 and 1228 cm^{-1} are assigned to C-C and C-O stretching. The symmetric stretching of -COO groups in oxalic acid gives signals at 1713 cm^{-1}, the band at 2988 cm^{-1} is originated from the stretching vibrations of -OH groups (21).

UV-Vis Spectra Analysis

Figure 11 displays the UV-Vis scanning curves of acetone + Na_2SO_4 solution (a), oxalic acid solution (b), oxalic acid + Na_2SO_4 solution (c) and acetone + Na_2SO_4 solution + electrocatalytically synthesized oxalic acid (d). It can be seen clearly that pure oxalic acid exhibits stronger absorption in the ultraviolet region at 200~220 nm, but no absorption in the visible region, which is in good agreement with electrocatalytically synthesized oxalic acid. Due to the presence of acetone, there is a strong optical absorption band at 264 nm as reported elsewhere (16).

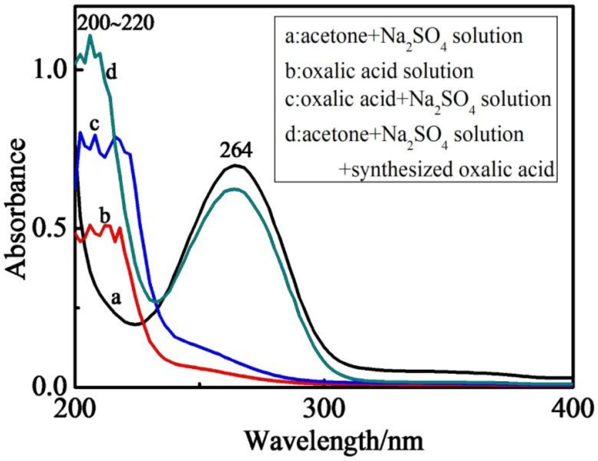

Figure 11. UV-Vis. absorption spectra of pure and electrocatalytically synthesized oxalic acid.

Reaction Mechanism

Electrocatalytic oxidation of acetylene to oxalic acid may occur by direct electron transfer (ET) at Pt electrode surface or by electrocatalytic oxidation (ECO) depending on the nature of the anode. It can be envisaged that adsorbed acetylene (Eq. 1) (22) is first oxidized to ethylene glycol (Eq. 3), which may then undergo a second ET to produce a very unstable transition state (Eq. 4) (8). By virtue of the electrostatic repulsions between the electrode and the transition state, the latter desorbs from the Pt electrode surface (Eq. 5). In this case, any oxygen donor available in Na_2SO_4 solution, for example H_2O, O_2 especially OH· is likely to be formed at the Pt electrode surface, followed by desorption. Alternatively, oxalic acid can be the result of ECO (Eq. 7). This mechanism is based on the formation of activated adsorbed acetylene and oxygen arising from any oxygen donor in Na_2SO_4 solution. What's more, it has been studied systematically in experiment, theory and quantitative calculation as reported in our previous research results (6, 23).

$$\mathrm{HC \equiv CH + Pt_s \rightarrow Pt\,(HC \equiv CH)_{ads}} \qquad (1)$$

$$\mathrm{Pt_s + H_2O - e^- \rightarrow Pt\,(OH\cdot)_{ads} + H^+} \qquad (2)$$

$$\mathrm{Pt\,(HC \equiv CH)_{ads} + 2Pt\,(OH\cdot)_{ads} \rightarrow Pt\,(OHCH{=}CHOH)_{ads} + 2Pt_s} \qquad (3)$$

$$\mathrm{Pt\,(HOCH{=}CHOH)_{ads} - 2e^- \rightarrow Pt\,(OHC\text{-}CHO)_{ads} + 2H^+} \qquad (4)$$

$$\mathrm{2Pt\,(OH\cdot)_{ads} + Pt\,(OHC\text{-}CHO)_{ads} \rightarrow 2Pt_s + Pt\,(HOOC\text{-}COOH)_{ads} + 2H^+} \qquad (5)$$

$$\mathrm{Pt\,(HOOC\text{-}COOH)_{ads} \rightarrow Pt_{ads} + (HOOC\text{-}COOH)} \qquad (6)$$

$$\mathrm{CH \equiv CH + 4H_2O - 8e^- \rightarrow HOOC\text{-}COOH + 8H^+} \qquad (7)$$

Conclusions

Electrocatalytic oxidation of acetylene to oxalic acid at Pt electrode in 0.5 M Na_2SO_4 with acetone (2% by volume) is a viable new strategy and offers several advantages over other traditional methods. Under the new condition, strong conditions such as high temperature and high pressure are not essential. Conversion occurs under mild experimental conditions; no need for a supply of O_2 and, above all, electrocatalytic synthesis can be performed in-site in 0.5 M Na_2SO_4 with acetone (2% by volume). The conversion efficiency is more than 20%. The electrochemical behavior of electrocatalytic oxidation of acetylene to oxalic acid in Na_2SO_4 has been examined by CV. The results show that the E_a of electroctalytic oxidation reaction of acetylene at Pt electrode is 14.42 $kJ\cdot mol^{-1}$, and the electrocatalytic oxidation processes of acetylene in Na_2SO_4 at Pt electrode are irreversible and under adsorption control. In addition, the reaction mechanism of the electrocatalytic oxidation process of acetylene to oxalic acid has been envisaged successfully based on the principle of adsorption and desorption at Pt electrode surface. By integrating the experimental data with theoretical knowledge, valuable guidance for the process of electrocatalytic synthesis of oxalic acid from acetylene can be achieved.

Acknowledgements

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