

Synthesis of L-Cysteine and L-Cysteic Acid by Paired Electrolysis Method

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L-Cysteine and L-cysteic acid were synthesized by paired electrolysis method. A high purity over 98% and high yield over 90% of both products were gained. When current density was 7 A/dm² and concentration of L-cysteine was 0.6 mol/dm³, the highest current efficiency of anode and cathode was achieved. Total current efficiency was over 180%. The cyclic voltammetry behaviors of hydrobromic acid and cystine showed that a typical EC reaction took place in the anodic cell. The anode reaction and successive chemical reaction accelerated each other to get a high speed and current efficiency.

L-Cysteine and L-cysteic acid are important biochemical reagents that are widely used as additives for medicine, forage and detergent.¹⁻³ At present most manufacturers produced L-cysteine from L-cystine by electrolysis method in which process only cathodic reaction was utilized while oxygen was given out from anode. As a result, electricity was not fully used and the product was single. L-Cysteic acid was often synthesized by oxidizing L-cystine with hydrogen peroxide, bromine or dimethyl sulphoxide with a low yield below 80%. In this article, L-cysteic acid and L-cysteine were simultaneously synthesized from L-cystine in the electrolytic cell by paired electrolysis method. This kind of paired electrolysis method can raise current efficiency and yield per unit volume of electrolytic cell at a fixed time so that production cost can be reduced strikingly. It has been adopted in preparing many useful fine chemicals such as gluconate, mannitol, sorbitol, succinic, and glyoxylic acid.^{4,5}

The experiment was conducted as follows: 0.6 mol/dm³ L-cysteine solution dissolved in hydrochloric acid and 0.6 mol/dm³ L-cysteine solution dissolved in hydrobromic acid were poured into cathodic and anodic cells of the self-made H-style electrolytic cell, respectively. The cathodic and anodic cells were connected with magnet pump through plastic pipe so that cathodic and anodic solutions circulated continuously. Graphite was adopted as electrodes in the electrolyzing process. Keeping current density to be 7 A/dm² and temperature to be 40 °C, constant current electrolysis was conducted. The reaction end was indicated by following changes of optical activity in electrolyte. After electrolysis the solutions from anodic and cathodic cells were condensed through vacuum distillation while hydrochloric and hydrobromic acids were recovered during the process. L-Cysteine and L-cysteic acid were obtained through washing, crystallizing, and drying the remainder after vacuum distillation. Both in the cathodic cell and anodic cells the actual yields were over 90% while purity over 98%.^{6,7} Electrochemical experiments were performed in a three-compartment cell with Pt as the counter electrode. A saturated calomel electrode (SCE) was the reference electrode while Pt sealed with glass was the study electrode with an area of 0.00785 cm². Cyclic voltammograms were obtained with a model 273 potentiostat/galvaostat,

HB-104 signal generator and a YEW3086 X-Y recorder. GM 388 alternating impedance system and M270 cyclic voltammetry software were used in the study of electrochemical behavior. The instruments were supplied by Park Cooperation of USA.

Reactant L-cystine ($[\alpha]_D^{20} = -219 \pm 5^\circ$) possess the opposite optical activity from the products L-cysteine ($[\alpha]_D^{20} = +6.5 \pm 1^\circ$) and L-cysteic acid ($[\alpha]_D^{20} = +8.6 \pm 1^\circ$). Consequently optical activity of both cathodic and anodic electrolytes changed markedly during the electrolyzing process. Determining optical activity of the electrolyte could monitor the reaction course and controll the electrolysis end.

Current efficiency at different current density and reactant concentration was tested. The results at anode and cathode were shown in Figures 1 and 2.

Experiments showed that reactions in anode and anodic electrolytes were almost ideal with high speed. Accordingly factors such as current density and reactant concentration had little influence on its current efficiency. The cathodic product was inclined to take place side reaction so the cathodic reaction reached its highest efficiency only when the electrode reaction

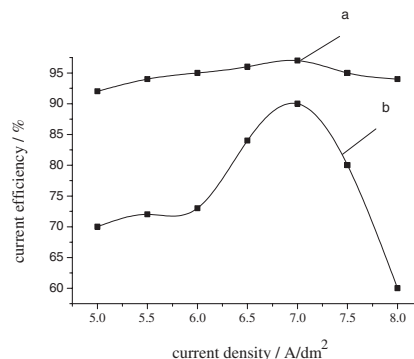


Figure 1. Effect of current density on current efficiency. (a) anode, (b) cathode.

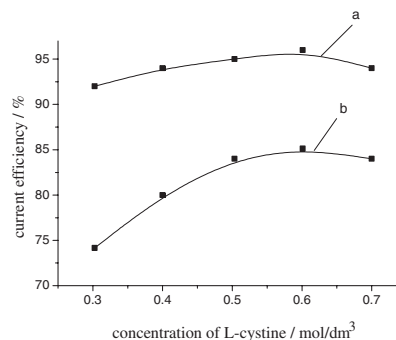
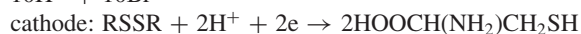
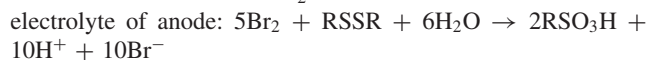
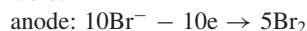


Figure 2. Effect of concentration of L-cystine on current efficiency. (a) anode, (b) cathode.

speed matched with experiment condition. Keeping current density to be 7 A/dm^2 , concentration of L-cystine to be 0.6 mol/dm^3 , current efficiency of both anode and cathode was maximum with an overall current efficiency over 180%.

Electrode reaction and chemical reaction in the electrolytes were:



During the electrolyzing process, Br_2 generated from anode reacted immediately with L-cystine to turn into L-cysteic acid and HBr. There was no accumulation of Br_2 which could be verified by the colorless electrolyte before reaching the electrolyzing end. After the complete reaction of L-cystine, Br_2 generated from anode would not be consumed which resulted in the yellow electrolyte.

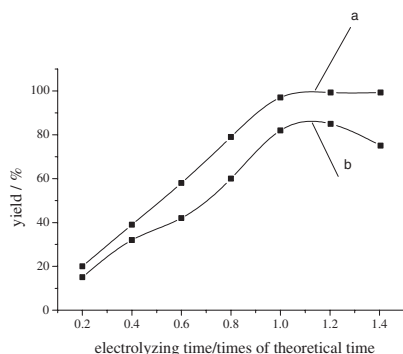


Figure 3. Effect of electrolyzing time on the yield. (a) anode, (b) cathode.

As it was shown in Figure 3 the product yields at anode and cathode increased linearly before the time of theoretic electrolyzing time. Prolonging the electrolyzing time had little influence on the anodic product but had bad influence on the cathodic product which resulted in decrease of yield of the cathodic product. Accordingly, electrolysis should be terminated at the completion of cathodic reaction. By adjusting mass concentration the anodic reaction should be made to reach its terminal before that of cathode.

In addition we had also studied other factors including the reaction temperature, flow rate of the electrolyte, and concentration of HBr and HCl. Higher reaction temperature was in favor of dissolving the raw materials and the products but would reduce the life time of ion-exchanging membrane which was key part of the electrolytic cell. Higher electrolyte flow rate would decrease concentration polarization and raise current efficiency but would also affect the lifetime of ion-exchanging membrane. Concentration of HBr and HCl had little effect on the reaction so enough HBr and HCl were used to dissolved L-cystine.

Electrochemical theory of the cathodic reaction has been well investigated elsewhere. Consequently we only studied the preliminary electrochemical behavior of the anodic reaction here. Solution of hydrobromic acid, L-cystine, both hydrobromic

acid and L-cystine were tested on their cyclic voltammetry behaviors. Their cyclic voltammetry behaviors under the same scanning rate and scanning scope were given in Figure 4.

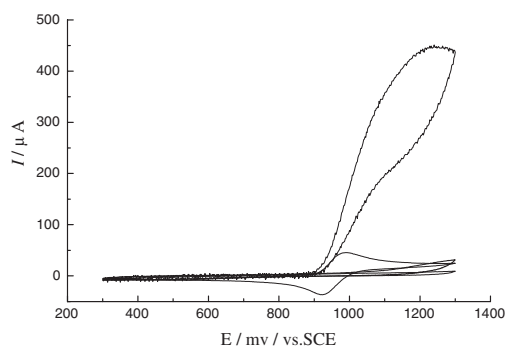


Figure 4. Cyclic voltammetry curves. Peak current decrease following the series of 10 mmol/dm^3 HBr + 0.1 mol/dm^3 L-cystine, 10 mmol/dm^3 HBr, 0.1 mol/dm^3 L-cystine, 0.5 mol/dm^3 H_2SO_4 .

As it could be concluded from Figure 4, reducing peak of bromine was found in HBr solution without L-cystine. After the addition of L-cystine into hydrobromic acid, oxidation current increased strikingly while there was no reducing peak of bromine during the reverse scans. Conclusion could be drawn from the cyclic voltammetry behaviors that it was a typical EC catalytic process. In the reaction system, as an oxidation media, HBr was first oxidized to Br_2 which reacted immediately with L-cystine to produce L-cysteic acid and bromide ion which would be oxidized to Br_2 once again on the anode. Above process circulated and accelerated reciprocally and resulted in the prompt and quantitative reaction.

In conclusion, L-cysteine and L-cysteic acid were synthesized by paired electrolysis method. The yields at anode and cathode were both over 90% while products purity was above 98%. Keeping current density to be 7 A/dm^2 , concentration of L-cysteine to be 0.6 mol/dm^3 , current efficiency of both anode and cathode reached their maximum value with an overall current efficiency above 180%. Cyclic voltammetry behaviors showed that a typical EC catalytic process took place in the anodic cell. The anodic reaction and the successive chemical reaction accelerated reciprocally which resulted in rapid reaction and high current efficiency.

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