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Electroreduction of cyanoacetic acid

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A simple electrolytic reduction method for the preparation of beta-alanine hydrochloride using deposited palladium black over graphite is described. Beta-alanine is used for the synthesis of vitamin 'pantothenic acid'. This electroreduction technique should be generally useful for the preparation of primary amines.

1. Introduction

Amino acids are useful drug intermediates. A number of alpha- and beta-amino acids are being used for the manufacture of a variety of drugs.

In the course of our reduction studies of various organic nitriles, it was decided to examine the use of deposited palladium black on a graphite cathode for the reduction of cyanoacetic acid and thus evolve a simple method for the preparation of beta-alanine. This reduction technique has been successfully employed for the preparation of various primary amines [1–4] from the corresponding nitriles. It does not require the use of high pressure storage of hydrogen or reactors and is easy to carry out. Among the methods available for the preparation of beta-alanine, two industrial methods are described in the literature starting from ethylene cyanohydrine [5] and acylonitrile [6]. In the present paper, the details of the experiments on the electroreduction of cyanoacetic acid to beta-alanine hydrochloride using the palladium black cathode are described. An Indian patent has been applied for to cover this process [7].

$$NC\,CH_2\,COOH \xrightarrow[\text{in acid medium}]{4H^+ + 4e}$$

$$HCl\,H_2NH_2C\,CH_2\,COOH$$

2. Results and discussion

2.1. *Deposition of palladium black on a graphite plate substrate*

500 ml of 10% aqueous HCl containing 0·4 g palladium chloride and 10 g ammonium chloride were used as the catholyte. 230 ml of 10% aqueous HCl, placed inside a ceramic porous pot, was used as the anolyte. The anode is a graphite plate of 0·6 dm ^{2} area. Graphite plates whose immersion depths in the plating solution corresponded to an effective area of 2 dm^2, were used as the cathodes on which palladium black was deposited. The catholyte was given a gentle stirring using a glass stirrer. The current density employed for deposition was 500 mA cm^{-2}

Palladium black was deposited on a rotating cylindrical graphite rod in the same way.

2.2. *Galvanostatic polarization measurement studies under stationary conditions*

In an aqueous hydrochloric acid solution as catholyte, cathode potential measurements were carried out using the deposited palladium black cathode both in the presence of cyanoacetic acid and in its absence. A saturated calomel electrode was used as the reference electrode. Aqueous hydrochloric acid and a graphite plate were used as the anolyte and anode respectively. A ceramic porous pot was used as the diaphragm. Fig. 1 gives a plot of cathode potential (mV) versus current density in a semi-logarithmic form. From the graph it is obvious that there is a considerable depolarization at low current densities. At higher current densities there is less depolarization leading to more hydrogen evolution. Galvanostatic polarization measurements with rotating cathodes yielded similar results. It is well-known that the surface of the deposited palladium black is saturated with hydrogen atoms and so the

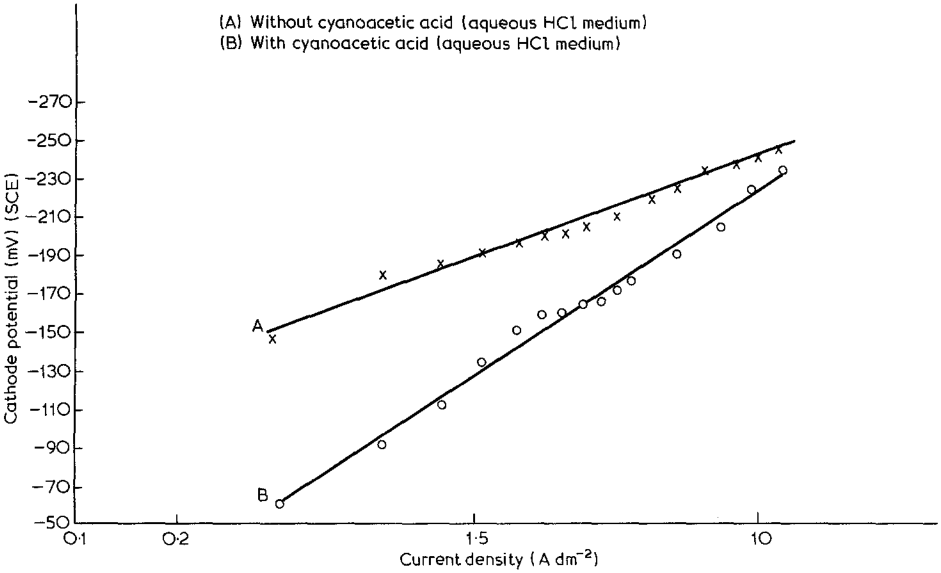

Fig. 1. Galvanostatic polarization study using deposited palladium black on graphite cathodes (stationary condition).

reduction of this nitrile group is mainly due to the chemisorbed hydrogen atoms. Since this reduction is not a diffusion-controlled process, the rotating electrode technique did not have any advantage over a stationary electrode technique.

2.3. *Reduction of cyanoacetic acid to beta-alanine hydrochloride*

8 g of cyanoacetic acid was dissolved in a catholyte of 10% aqueous hydrochloric acid. 230 ml of 10% aqueous hydrochloric acid as anolyte was placed in a ceramic porous pot containing the graphite plate anode. Two cathodes of palladium black deposited on graphite plate (effective area 2 dm^2) were placed opposite the diaphragm. The catholyte was stirred by means of a glass stirrer and the temperature of the catholyte was maintained at around 15–20° C. A current of 4 A was passed (current density 2 A dm^{-2}) at a cell voltage of 2·2 V. As the theoretical charge was insufficient to complete the reaction, extra current was passed. At the end of the electrolysis, the catholyte was vacuum distilled to obtain a brown solid. This solid was purified by dissolving it in the minimum amount of absolute ethanol necessary and reprecipitating it by the addition of ether. (8·6 g; yield 73%; current efficiency 36·5%).

A number of such reduction experiments under similar conditions were carried out at different current densities ranging from 1 to 15 A dm^{-2}. In all these cases more than the theoretical current was passed to obtain a good yield of beta-alanine hydrochloride. From Table 1, it is clear that high yield and current efficiencies are obtained only at the lower current densities.

2.4. *Preparation of beta-alanine hydrochloride on a 50 A scale*

For the 50 A scale, a hollow cylindrical graphite vessel with palladium black deposited on the inside was used as the cathode. The outside of the graphite vessel was coated with Araldite to prevent the oozing of the catholyte through the pores of the graphite. The graphite vessel (effective area 8 dm^2) itself acted as the container as well as cathode. 100 g of cyanoacetic acid was taken in a

Table 1.

Current density (A dm^{-2})	*Yield* (%)	*Current efficiency* (%)
1	75	37·5
2	73	36·5
5	63	31·5
10	50	25
15	45	22·5

supporting electrolyte of 1·3 l of 10% aqueous hydrochloric acid. 800 ml of 10% aqueous hydrochloric acid was used as the anolyte. The catholyte and the anolyte were separated by means of a ceramic porous pot kept in the middle of the graphite vessel. Twice the theoretical charge was passed to effect maximum conversion of the reactant. 100 g of cyanoacetic acid gave 70 g of beta-alanine hydrochloride (yield 50%; current efficiency 25%).

Further work is in progress for scaling up the process to a still higher amperage capacity.

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