This invention relates to the preparation of Beta-alanine hydrochloride electrochemically from cyanoacetic acid using deposited palladium black graphite cathodes (both stationary and rotating).

Hitherto, the following methods have been proposed for the preparation of Beta-alanine: (i) Reduction of cyanoacetic acid using reagents such as sodium-ethanol, Raney Nickel and Lthium aluminium hydride; (ii) Condensation of chloracetic acid with ammonia in presence of ammonium chloride; (iii) Electrochemical reduction of cyanoacetic acid using deposited palladium over platinum electrodes. In the third method, it has been reported that the yield of Beta-alanine is very poor and the palladium deposit over platinum is not adherent and hence a fresh deposit was found to be necessary for each experiment.

The method developed by us at present is a simple electrochemical route which gives a good yield of Beta-alanine in pure state. This invention consists of two stages. The first stage involves the deposition of palladium black over graphite cathode using a bath containing

palladium chloride and ammonium chloride in aqueous hydrochloride acid medium. The current density employed for the deposition is very low. Aqueous hydrochloric acid contained in the porous pot is used as the anolyte, the anode being a graphite plate.

The second stage involves the electro-reduction of cyanoacetic acid in aqueous hydrochloric acid medium using deposited palladium black over graphite cathode, both under stationary and rotating conditions. A graphite anode is kept inside a ceramic porous pot, aqueous hydrochloric acid being the anolyte. The reduction is carried out in the temperature range of 8 to 12°C. In these cases where cathode is kept stationary, the catholyte is vigorously stirred using a glass stirrer. A current density of 2-4 A/sq.dm. can be employed for the reduction of both stationary and rotating systems. Nearly twice the theoretical time has been found to be necessary for obtaining a good yield. After the electrolysis is over, the catholyte is distilled under vacuum to complete dryness, when a pale brown solid of Beta-alanine hydrochloride was obtained. This was further purified by dissolving in absolute ethanol and precipitating by dry ether.

The following are the typical examples to illustrate the invention:

PART I Deposition of palladium black over graphite(stationary)

Cathode	: Graphite plate
Anode	: Graphite placed inside a diaphragm
Catholyte	: A dilute solution of palladium chloride (1 gpl) in aqueous HCl 6% (w/v) containing 0.5 to 2% ammonium chloride (Total Volume 350 ml)
Anolyte	6% aqueous HCl (w/v) (75 ml)
Cathode current density	50 mA/sq.dm.
Anode current density	75 mA/sq.dm.
Cell voltage	1.5
Temperature	30-35°C

The deposition is continued till the catholyte becomes colourless. The same procedure is adopted for the deposition of palladium black over rotating cylindrical graphite rod.

PART II(A) Reduction of cyanoacetic acid using stationary cathode

Catholyte	: 10% aqueous hydrochloric acid(500 ml)
Anolyte	: 10% aqueous hydrochloric acid(230 ml)
Cathode	: Palladium black deposited over graphite plate (effective area 2 sq.dm.)
Anode	: Graphite plate (0.6 sq.dm.)
Current passed	: 4 amperes
Cell voltage	: 2.4
Temperature of the cell	: 8-12°C
Cyanoacetic acid taken	: 8 gms
Beta-alanine hydrochloride isolated	: 8 gms
Yield efficiency	: 68%
Current efficiency	: 34%
Energy consumption	: 6.05 kWh/kg

PART II(B) Reduction of cyanoacetic acid under rotating conditions

Catholyte	: 10% aqueous hydrochloric acid(500 ml)
Anolyte	: 10% aqueous hydrochloric acid(230 ml)
Cathode	: Palladium black deposited over rotating cylindrical graphite rod (effective area 1 sq.dm.)
Anode	: Graphite plate (0.6 sq.dm.)
Current passed	: 2 amps
Voltage	: 2.4 V
Temperature of the cell	: 8-12°C
Cyanoacetic acid taken	: 4 gms
Beta-alanine hydrochloride isolated	: 3.75 gms
Yield efficiency	: 60%
Current efficiency	: 30%
Energy consumption	: 6.86 kWh/kg

The following are the main features of the invention:

1. This invention opens up a new and simple route for the synthesis of Beta-alanine.

2. A thinly deposited surface was found to be enough for carrying out the reduction of cyano acetic acid.

3. This method avoids the use of solvents like ethanol and high pressure generating equipment whibh are essential for catalytic methods.

Dated this 7th day of November 1974

1. Dr.H.V.K.Udupa, Director

2. Sd/- Dr.V.Krishnan, Scientist

3. Sd/- Shri K.Ragupathy, Jr.Scientific Asst.

Dated this 19th day of April, 1975

Sd/-
Asstt.Patents Officer,
Council of Scientific & Industrial Research

144404

THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

" IMPROVEMENTS IN OR RELATING TO THE ELECTROCHEMICAL PREPARATION OF BETA-ALANINE HYDROCHLORIDE FROM CYANOACETIC ACID "

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1 India, an Indian Registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :-

This is an invention by Handady Venkatakrishna Udupa, Director, Venkatasubramanian Krishnan, Scientist and Kanakasabapathy Ragupathy, Junior Scientific Assistant, all of Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India and all are Indian citizens.

This invention relates to the preparation of beta-alanine hydrochloride, a drug intermediate. This chemical has been so far prepared by the following methods: (i) Reduction of cyanoacetic acid using reagents such as sodium-ethanol, Raney nickel and lithium aluminium hydride, (ii) Condensation of chloroacetic acid with ammonia in presence of ammonium chloride, (iii) Electrochemical reduction of cyanoacetic acid using palladium electrode.

The process described in the specification is better than the chemical methods (i) and (ii) as it gives a pure product with a higher yield efficiency. Moreover, the invented electrochemical method of preparing beta-alanine hydrochloride is expected to be less costly compared to (iii), as only small amounts of palladium is deposited over graphite cathodes for reduction experiments.

The main object of the invention is to prepare pure beta-alanine hydrochloride in good yields. The first stage of the process is the deposition of palladium black over graphite cathode using an aqueous acid solution containing palladium chloride and ammonium chloride. These deposited palladium black cathodes were used for few reduction experiments with periodic replenishment of the deposit. Thus, this electroreduction technique involves the use of only small amounts of palladium.

The second stage of the process deals with the preparation of beta-alanine hydrochloride from cyanoacetic acid. In this method, deposited palladium black

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Deposition of palladium black over graphite cathode (Stationary)

Cathode	Cylindrical graphite vessel closed at one end
Anode	Graphite placed inside a diaphragm
Catholyte	A dilute solution of palladium chloride (2.5 gms) in aqueous HCl (6% w/v) containing around 0.4 to 0.8% ammonium chloride. The solution was vigorously stirred using a glass stirrer. Total volume = 1.5 litres
Anolyte	6% aqueous HCl
Cathode current density	50 mA/sq.dm.
Anode current density	75 mA/sq.dm.
Voltage	1.5 V
Temperature	30 - 35°C

Reduction of cyanoacetic acid: Experiment No.1

Catholyte	1.3 litres of 3 N aqueous hydrochloric acid
Anolyte	800 ml of 3N aqueous hydrochloric acid
Cathode	Palladium black deposited in the inner portion of the cylindrical graphite vessel closed at the bottom (effective area = 8 sq.dm.)
Anode	Graphite (area 6 sq.dm.) placed inside a diaphragm
Current passed	50 amps
Cell voltage	3.5 V
Temperature of the catholyte	20 - 25°C
Cyanoacetic acid taken	100 gms
Beta-alanine hydrochloride obtained	75 gms
Yield efficiency	50%
Current efficiency	25%
Energy consumption	12.0 kwh/kg

Experiment No.2

Catholyte	1.3 litres of 3N aqueous hydrochloric acid
Anolyte	800 ml of 3N aqueous hydrochloric acid
Cathode	Palladium black deposited in the inner portion of the cylindrical graphite vessel closed at the bottom (effective area = 8 sq.dm.)
Anode	Graphite (area 6 sq.dm.)placed inside a diaphragm
Current passed	50 amps
Cell voltage	3.5 V
Temperature of the catholyte	20-25°C
Cyanoacetic acid taken	100 gms
Beta-alanine hydrochloride obtained	77.5 g
Yield efficiency	62%
Current efficiency	31%
Energy consumption	7.7 kwh/kg

Advantages of this invention are as follows:

(i) By using a proper ratio of palladium chloride and ammonium chloride, a thin deposit of palladium black is obtained over graphite cathode and this cathode can be reused for a few reduction experiments.

(ii) There is no need for the purification of the cathode surface and hence practically there is no loss of precious metal. Thus this is highly advantageous over the catalytic method.

(iii) This reduction technique is a simple process and does not involve the use of high pressure generating equipment and other facilities for protecting the precious metal catalyst.

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We claim:

1) Improved electrochemical process for the preparation of Beta-alanine hydrochloride from cyanoacetic acid using a palladium electrode - characterised in that the electrode used consists of graphite on which a layer of palladium black is electrodeposited using an aqueous acid solution containing palladium chloride and ammonium chloride.

2) Process as claimed in claim 1 wherein the catholyte is distilled under reduced pressure and beta-analine hydrochloride is obtained as residue.

3) Improved electrochemical process for the preparation of Beta-alanine hydrochloride from cyanoacetic acid using a palladium electrode substantially as herein described.

Dated this 3rd day of May 1976

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Scientist'E' (Patents)
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

Nº OF SHEETS:- 1
SHEET Nº. 1

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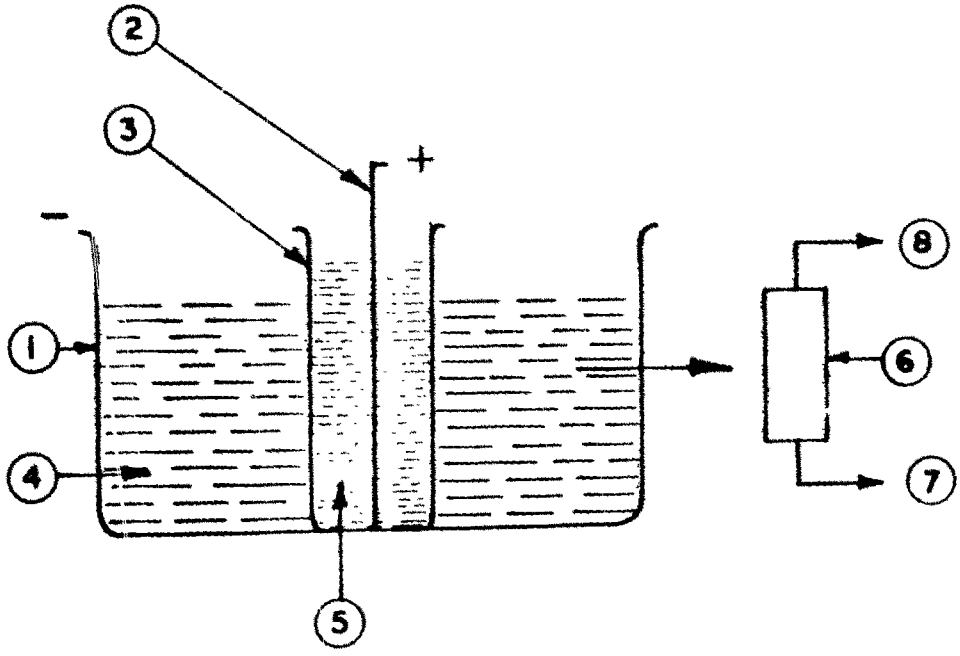

FIG. 1

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