JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 657–659

The electroreduction of benzyl cyanide on iron and cobalt cathodes

V. KRISHNAN, A. MUTHUKUMARAN, H. V. K. UDUPA
Central Electrochemical Research Institute, Karaikudi 623 006, India

Received 12 October 1978

An electrochemical method for preparing amines from organic cyanides using iron black and cobalt black cathodes has been studied. Benzyl cyanide underwent smooth reduction at a cobalt black cathode in an aqueous ethanolic ammonium sulphate medium to give a 74% yield of 2-phenylethylamine with a current efficiency of 50%; whereas with an iron black cathode under the same conditions, a 57% yield of 2-phenylethylamine has been obtained with a current efficiency of 33%.

1. Introduction

2-phenylethylamine is used in the drug industry. In view of the vast potential of amines, efforts were made in our laboratories to develop an economical method for its production, using different cathodes.

Studies on the electroreduction of organic cyanides to their primary amines using palladium black and nickel black deposited onto graphite cathodes have already been made [1–5]. As iron and cobalt also belong to the same group VIII, it was planned to examine the use of these cathodes as deposited black cathodes for the reduction of benzyl cyanide and to see whether the yield was improved.

$$C_6H_5CH_2CN \xrightarrow[\text{Fe black/Co black cathode in aqueous ethanolic } (NH_4)_2SO_4 \text{ medium}]{4H^+ + 4e}$$

$$\underset{\text{(main product)}}{C_6H_5CH_2CH_2NH_2} + \underset{\text{(small amounts)}}{(C_6H_5CH_2CH_2)_2NH}$$

2. Results and discussion

2.1. *Deposition of iron black and cobalt black onto a graphite plate substrate*

A plating solution containing 5 g of ferrous sulphate and 10 g of ammonium sulphate in 1·8 l of water was employed for deposition. Ceramic diaphragms, which were used as anode chambers, were filled with 10% aqueous sulphuric acid and fitted with lead anodes. A graphite plate was flanked on both sides with two diaphragms. The temperature of the plating bath was maintained between 20–25° C and the pH around 4·5–5·5. A current of 10 A (current density being 5 A dm^{-2}) at a cell voltage of 10–12 V was passed for 1 h 45 min. The iron black deposit obtained on graphite plate was used for the reduction experiments.

The deposition of cobalt black over graphite plate was carried out under the same conditions using a plating bath containing 5 g of cobalt sulphate and 10 g of ammonium sulphate in 1·8 l of water.

2.2. *Electroreduction of benzyl cyanide to 2-phenylethylamine using Fe black/Co black cathodes*

Details of the electrolysis are described in our earlier publications [1–5] but the conditions can be summarized as follows:

(a) The supporting electrolyte was made up of 630 ml alcohol, 560 ml water and 36 g $(NH_4)_2SO_4$.

(b) The amount of benzyl cyanide taken was 20·4 g.

(c) The anolyte was made up of 18 ml concentrated H_2SO_4 and 282 ml water.

(d) The anode was lead plates.

Excess current was passed in order to obtain the maximum yield of the product. After electrolysis, the catholyte was distilled to recover the

Table 1

Current density ($A\,dm^{-2}$)	*Cell voltage* (V)	*Yield of 2-phenylethylamine* (%)	*Current efficiency* (%)	*Secondary amine* (%)
with iron black cathodes				
2	6	57–60	33–35	10–12
5	8	57–60	33–35	10–12
8	14	48–50	25–27	10–12
with cobalt black cathodes				
2	6	72–74	48–50	10
5	8	72–74	48–50	8–10
8	12	72–74	48–50	8
12	15	50–52	25–26	4

alcohol. The remaining aqueous portion was extracted with organic solvent to remove the unreduced benzyl cyanide. The aqueous solution was then neutralized with NaOH and free amine was liberated. This amine was purified by distillation (boiling point 198° C). A small amount of product did not distill and this is the secondary amine. Table 1 gives us an idea of the yield and current efficiencies using iron black and cobalt black cathodes at different current densities.

2.3. *Galvanostatic polarization measurement studies*

In a supporting electrolyte of 1:1 aqueous ethanolic ammonium sulphate, cathode potentials were measured using deposited iron black and cobalt black cathodes separately, with a Philips VTVM. Cathode potentials were noted at different current densities both with and without benzyl cyanide. Fig. 1 gives a plot of cathode potential versus cur-

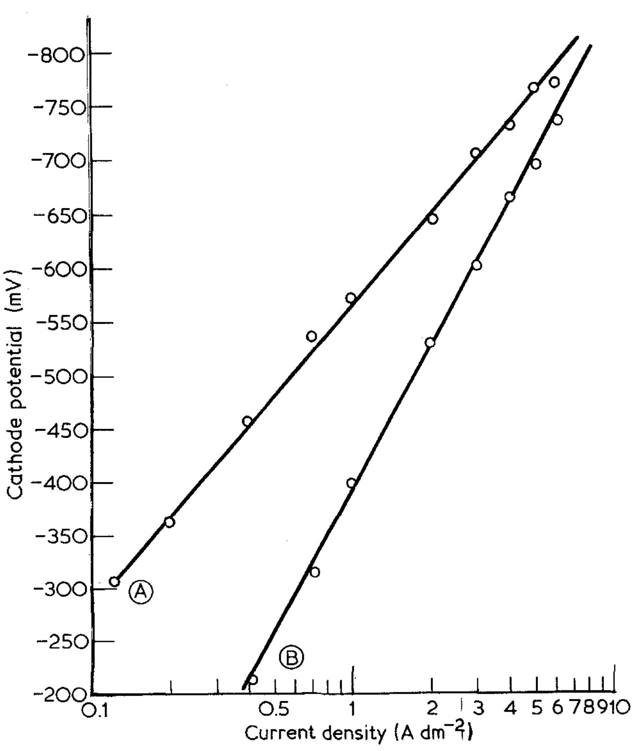

Fig. 1. Galvanostatic polarization curves using a deposited iron black cathode in an aqueous ethanolic ammonium sulphate medium. (A) without benzylcyanide, (B) with benzylcyanide.

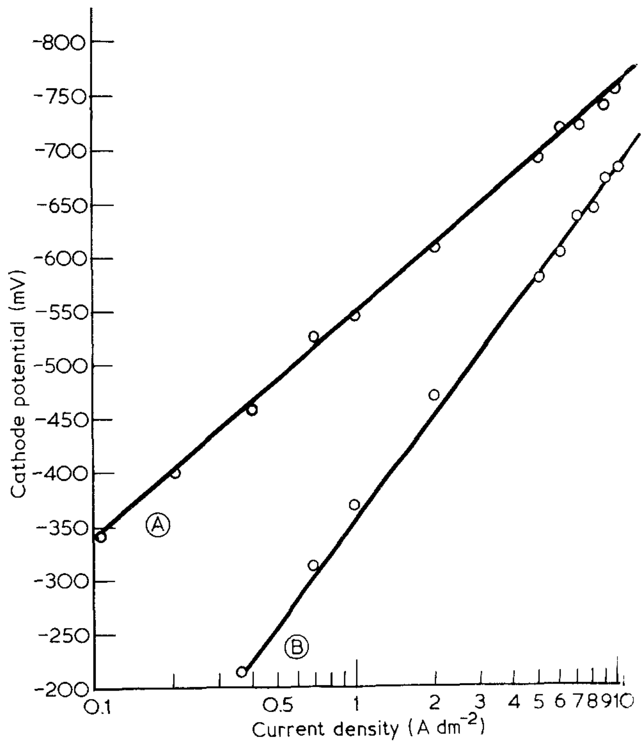

Fig. 2. Galvanostatic polarization curves using a deposited cobalt black cathode in an aqueous ethanolic ammonium sulphate medium. (A) without benzylcyanide, (B) with benzylcyanide.

rent density in a semi-logarithmic form for studies made with iron black cathodes. Fig. 2 relates the study made with cobalt black cathodes. From the graph it is obvious that there is a considerable depolarization only at low current densities for both these two electrodes. At higher current densities there is less depolarization leading to more hydrogen evolution. From Table 1 it is clear that higher yields and higher current efficiencies are obtained when the electrolyses are carried out at lower current densities. This is in agreement with the cathode potential measurement studies.

Based on the laboratory data the preparation of this amine on a pilot plant scale using Fe and Co cathode is in progress.

References

[1] V. Krishnan, K. Ragupathy and H. V. K. Udupa, *J. Appl. Electrochem.* **5** (1975) 125.

[2] *Idem, Electrochim Acta* **21** (1976) 449.

[3] V. Krishnan and H. V. K. Udupa, *Proceedings of the International Symposium on Industrial Electrochemistry*, SAEST India (1976) 251.

[4] V. Krishnan, K. Ragupathy and H. V. K. Udupa, *Trans. SAEST* **11** (1976) 509.