Electroreduction of p-Nitroaniline at Different Metal Electrodes

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Paranitroaniline has been electrolytically reduced to p-phenylenediamine at stationary nickel and copper amalgamated electrodes in aqueous sulphuric acid medium using galvanostatic method. Effect of different parameters such as current density, temperature, depolarizer ratio and nature of the cathode material has been studied to get the optimum conditions to obtain maximum yield.

The reduction of (o-, m- & p-) nitroanilines has been studied at gold amalgamated electrode[1]. The cathodic reduction of p-nitroaniline in alkaline as well as acidic media has been reported at amalgamated gold ring disk electrode[2,3]. p-Nitroaniline has been electrolytically reduced to p-phenylenediamine at mercury, and platinum[4] and copper[5] electrodes. Maximum yield of 95% is reported at platinum electrode. Gold and platinum are too costly for commercial preparations while mercury pool electrode creates environmental pollution problems.

p-Phenylenediamine is an excellent photographic developer. It can be easily diazotized and thus used in the manufacture of dyes. Ordinarily p-phenylenediamine is prepared by the reduction of p-nitroaniline with tin or iron and hydrochloric acid. Tin is more expensive and in case of iron the disposal of iron oxide sludge is a problem and yield depends on quality of iron powder employed. Further more in other chemical methods, yield is found in the range of 80 to 90%.

The electroreduction of p-nitroaniline has therefore been studied at nickel and copper amalgamated electrodes in aqueous sulphuric acid medium. Results are presented here. Effect of parameters such as current density, temperature, depolarizer ratio and the nature of the electrode material has also been studied.

EXPERIMENTAL

The electrolysis cell consisted of a 500 ml beaker (tall form, without spout) with the provision for stationary cathode (copper amalgamated or nickel), thermometer, magnetic stirrer bar and a porous pot which was used as anode diaphragm. Cathodes were used in stirrup shape. Anode was a lead sheet and had an area 40 cm^2 . Ceramic diaphragm was used to separate the anolyte from catholyte. Anolyte as well as catholyte used was 10% H_2SO_4 . Level of anolyte in ceramic diaphragm was put slightly higher than the catholyte in the cell. The cell was kept on a magnetic stirrer having hot plate which could be controlled according to requirements. The low temperature was controlled by ice cold water around the cell assembly.

A current regulated power supply (Developed by U.L.P in Physics, Univ. of Rajasthan, Jaipur) was used to apply different current densities across the working electrode (cathode) and the counter lead electrode (anode) and the corresponding potential of the working electrode vs SCE was measured by HIL Digital multimeter model 2142. Theoretical quantity of electric current for desired reaction was passed. After passing the current, the solution was filtered to recover decomposed mass if any. Solution was concentrated on waterbath, cooled in ice and then filtered. p-phenylenediamine sulphate separated out. It was washed with ice cold water for two or three times and then neutralized with 5% Na_2CO_3 or NaOH solution. P-Phenylenediamine was extracted with ether from the neutralized solution. Crude p-phenylenediamine obtained was purified by recrystallization.

RESULTS AND DISCUSSIONS

Polarization curves obtained by plotting potential vs log c.d. are given in Figs. 1 and 2. Different current densities were chosen from the polarization curves to investigate the proper current density at which yield is maximum.

From table 1 it can be easily inferred that favourable current density for the reduction under study are 0.0839 amp/cm^2 for copper (amalgamated) and 0.0412 amp/cm^2 for nickel electrode. Effect of parameters such as temperature and depolarizer ratio on percentage yield was now investigated and the results are summarized in table 2 and 3.

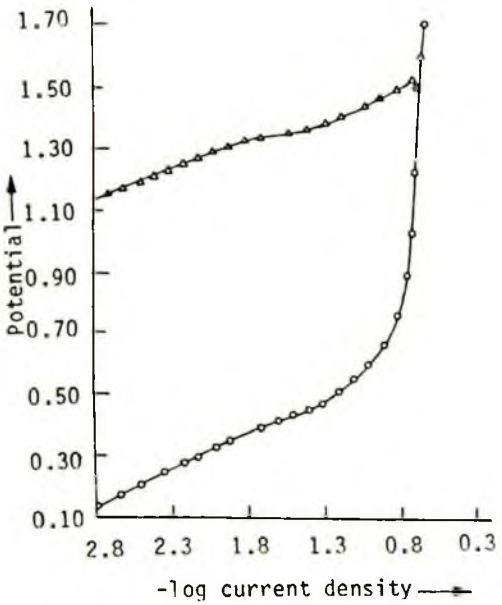


Fig.1 Cathodic Polarization curves at Copper amalgamated electrode.

Without Depolarizer (10% H_2SO_4)
With Depolarizer
(10% H_2SO_4 + p-Nitroaniline)

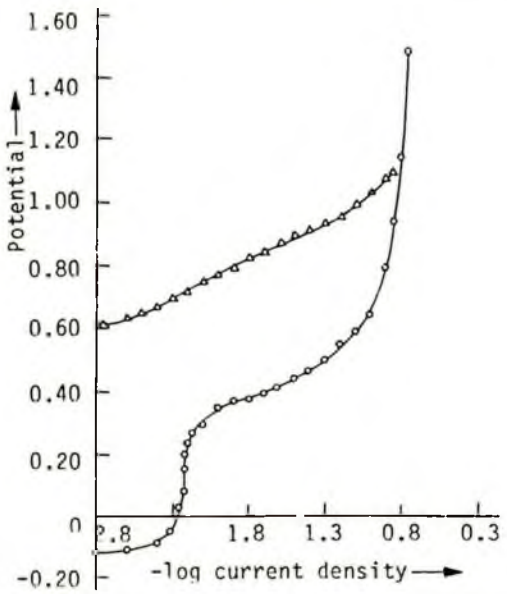


Fig.2 Cathodic Polarization curves at Nickel electrode.

Without Depolarizer (10% H_2SO_4)
With Depolarizer
(10% H_2SO_4 + p-Nitroaniline)

TABLE 1

EFFECT OF CURREENT DENSITY

T=(30±0.1)° Depolarizer ratio 1:40

S. No.	Electrode	Current Density Amp/cm²	Yield
1.	Amalgamated Copper cathode	0.1581	75.1
2.	Amalgamated Copper cathode	0.0839	84.6
3.	Amalgamated Copper cathode	0.0207	83.5
4.	Nickle Cathode	0.125	81
5.	Nickle Cathode	0.0412	89.7
6.	Nickle Cathode	0.0950	87.1

TABLE 2

EFFECT OF TEMPERATURE

Depolarizer ratio 1:40

S. No.	Electrode	Temperature (± 1)° C	Yield %
1.	Amalgamated Copper	15	80.5
2.	Cathode at I=0.0839	30	84.6
3	Amp/Cm²	45	91.6
4.	Nickle Cathode	15	86.0
5	0.0412 Amp/cm²	30	89.7
6	— —	45	92.6

TABLE 3

EFFECT OF DEPOLARIZER RATIO

T = 45 ± 1°C

S. No.	Electrode	Current Density Amp/cm²	Depolarizer ratio	Yield %
1	Copper (amalgamated)	0.0839	1:50	72.5
2	--	--	1:40	91.6
3	--	--	1:30	94.5
4	Nickel	0.0412	1:50	65.0
5	--	--	1:40	92.6
6	--	--	1:30	93.6

It is clear from the results that under optimum conditions the yield of p-phenylenediamine is arround 95% using easily available cheap metal electrodes and an aqueous sulphuric acid medium.

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