CATHODE MATERIAL IN THE ELECTROSYNTHESIS OF p-AMINOPHENOL FROM NITROBENZENE— VOLTAMMETRIC APPROACH

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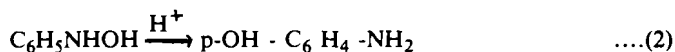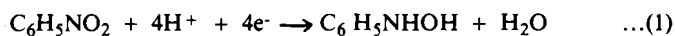Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

Voltammetric studies of nitrobenzene reduction on Cu, glassy carbon (GC) and Pb electrodes were carried out with a view to ascertain the choice of cathode material for p-aminophenol synthesis. Lead was found to give irreproducible responses due to some electrochemical mixed potential processes. However, on Cu and GC electrodes, the electroreduction was found to stop at the four electron stage in the first peak potential region which indeed is the condition required for phenylhydroxylamine formation. This conclusion was drawn based on voltammetric peak current calculations as well as the comparative voltammetric studies of nitrobenzene and p- nitrophenol which is known to follow a 6 electron path. Comparing the voltammetric curves on Cu and GC for nitrobenzene in alcoholic H_2SO_4 medium, it is noticed that the hydrogen evolution process starts at much more positive potentials on Cu as compared to GC. Since further reduction of phenyl hydroxylamine to the aniline along with H_2 evolution would also occur on Cu, it is concluded that carbon electrode would be a better choice for p-aminophenol synthesis.

Key words: Linear sweep voltammetry, p-aminophenol, nitrobenzene reduction

INTRODUCTION

Preparation of p-aminophenol from nitrobenzene is certainly one of the attractive processes in synthetic electro-organic chemistry. This reaction proceeds by formation of 4e reduction product— phenyl hydroxylamine at the electrode surface and subsequent para transformation of this in the acidic electrolyte medium.

$$C_6H_5NO_2 + 4H^+ + 4e^- \longrightarrow C_6H_5NHOH + H_2O \qquad ...(1)$$

$$C_6H_5NHOH \xrightarrow{H^+} p\text{-}OH \cdot C_6H_4 \text{-}NH_2 \qquad ....(2)$$

Because of the potential commercial application, many investigations have been carried out to optimise this process over a long period of time [1-9] and these efforts have also been reviewed from time to time [10,11]. In spite of these efforts, difficulties still exist. The main problem is a competitive electrochemical reaction to the chemical reaction (2).

$$C_6H_5NHOH + 2H + 2e^- \longrightarrow C_6H_5NH_2 + H_2O \qquad ...(3)$$
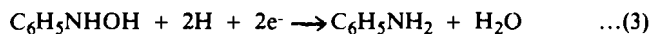
This results in the formation of a large quantity of aniline along with the desired p-aminophenol, leading to lowering of the yield as well as difficulty of separation. Efforts were made by varying different parameters such as temperature of electrolysis, current density, addition of different inorganic salts, current interruption during electrolysis and using alcoholic and isopropanolic H_2SO_4 medium with the primary objective of minimising the influence of the side reaction (3). Surprisingly, however, in all these investigations [1-11] copper or amalgamated Cu alone has been used as the cathode. The influence of electrode material itself has not received sufficient attention.

In the present work an attempt has been made to investigate the voltammetric behaviour of nitrobenzene on Cu, Pb and Glassy Carbon (GC) cathodes to find out the influence of each of the cathodes. Direct reduction of p-nitrophenol on these cathodes was also investigated to understand the reaction pathways.

EXPERIMENTAL

Electrical grade copper rod, (6mm dia) GC rod (5mm dia) and high purity lead rod (6mm dia) fixed to a teflon rod were used as working electrodes. The Cu cathode was cleaned with trichloroethylene and cathodically polarised for a few minutes before use [12]. For lead cathode great care was taken not to retain the electrode in the 2.0M H_2SO_4 electrolyte for longer time, to ensure reproducibility as discussed earlier [13]. The potential cycling procedure recommended earlier [14] was employed for GC electrodes. Nitrobenzene, p nitrophenol and H_2SO_4 (all analytical grades) were used. All the experiments were carried out at $298 \pm 0.5K$. All other details regarding H-type cell, deaeration of electrolyte and instrumental set up employed have already been discussed [12].

RESULTS

It is a well known fact that Pb in H_2SO_4 medium would spontaneously form $PbSO_4$ layer. This process would lead to time-dependent irreproducible voltammetric behaviour. In the case of voltammetric reduction of phthalic acid [13] this process was avoided by carefully controlled experiments. Similar efforts were made in the present experiment using nitrobenzene as well. However since nitrobenzene reduction starts at potentials more positive than -0.650V vs SCE where $PbSO_4$ film formation/reduction effects cannot be avoided, proper voltammetric investigation of this compound was practically impossible. Hence after preliminary investigations, subsequent experiments were mostly confined to Cu and GC cathodes.

Typical linear sweep voltammograms (LSV) of nitrobenzene (NB) at copper electrodes in 2.0M H_2SO_4 at various sweep rates are presented in Fig.1. A single well-defined irreversible cathodic peak,

was noticed. The peak current ip was proportional to square root of sweep rate, $V^{1/2}$ and concentration of nitrobenzene, C_{NB}. In these respects, the voltammetric behaviour is similar to the one reported earlier [15].
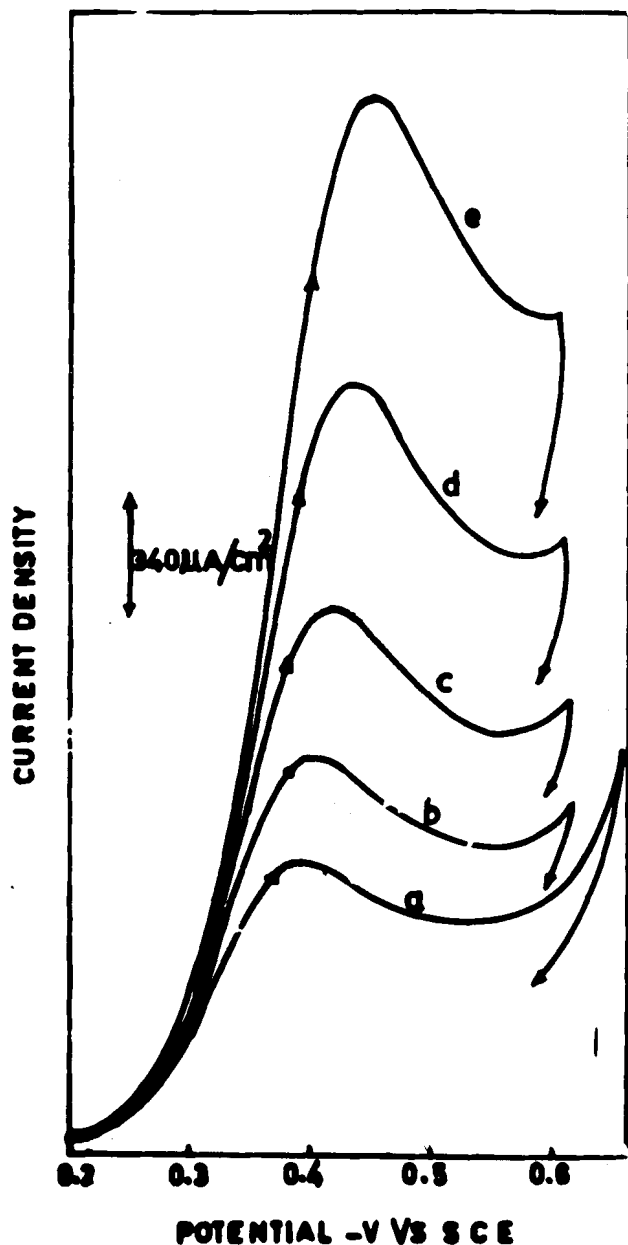

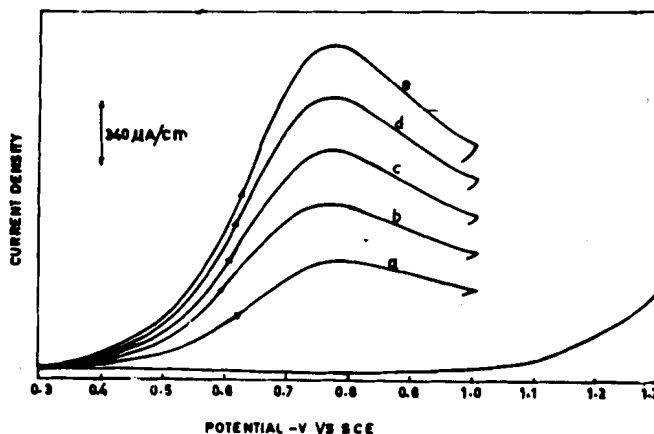*Fig. 2: L S V of nitrobenzene at G C electrode in 2 M H_2SO_4 at a sweep rate of 40 mV.s⁻¹ at various concentrations of NB (mM) (a) 1, (b) 1.5, (c) 2, (d) 2.5 and (e) 3.0*

The peak potential (Ep) values however are quite different for these two electrodes. The slope of the rising portion of the voltammogram is also different. The experimental peak current constant (Ip) values (Ip = i_p/ACV) where A is the area of the electrode, are also different. These values are tabulated in Table I.

Typical LSV curves of p-nitrophenol (PNP) on GC electrode at different concentrations are presented in Fig.3. The voltammograms are qualitatively similar. But the quantitative features are again different as shown in Table I. The voltammetric response of PNP on Cu cathode is also compared in Table I.

The LSV responses of nitrobenzene and PNP on GC electrodes are compared under identical conditions in Fig.4. The voltammograms of PNP show higher heights when compared to nitrobenzene. The slope of the curve also is substantially higher. In 2.0M H_2SO_4 medium, H_2 evolution starts on copper around -0.65V (Fig.1 background) whereas this process is not at all intiated upto -1.25V on GC cathode. Up to this potential region no further reduction is noticed on GC cathode.

Fig.1: L S V of nitrobenzene (1mM) at copper electrode in 2M H_2SO_4 at different sweep rates (mV.s⁻¹) (a) 20, (b) 40, (c) 80, (d) 160 and (e) 320

Typical LSVs of nitrobenzene on GC cathode at different concentrations are presented in Fig.2. The voltammetric behaviour is qualitatively similar. i_p is proportional to V ½ as well as C_{NB}.

DISCUSSION

The voltammetric behaviour of nitrobenzene on GC has already been discussed [15]. The transfer coefficient of irreversible charge transfer can be calculated using equation (4).

$$E_p - E_{p/2} = \frac{48}{\alpha\,na} \qquad ...(4)$$

Since the transfer coefficient values in all the four cases investigated here are around 0.5, it may be inferred that the first electron transfer is the rate determining step in all the cases. Hence the following expression defines the peak current constant values [16].

TABLE-I: Voltammetric behaviour of nitrobenzene (NB) and p-nitrophenol (PNP) on Cu and G.C. electrodes

Sl.No	Electrode	Compound	$-E_p$ (mV)	I_p (mA)	n_a	n	$-E_H$ (mV)
1	G.C.	NB	630	2630	0.3428	4.35	1250
2	Cu	NB	380	3602	0.6400	4.36	650
3	G.C.	PNP	775	3043	0.2740	6.00	1250
4	Cu	PNP	485	3550	0.4800	5.30	650
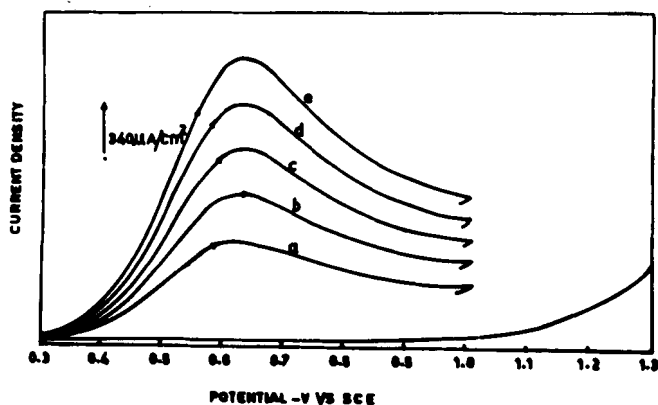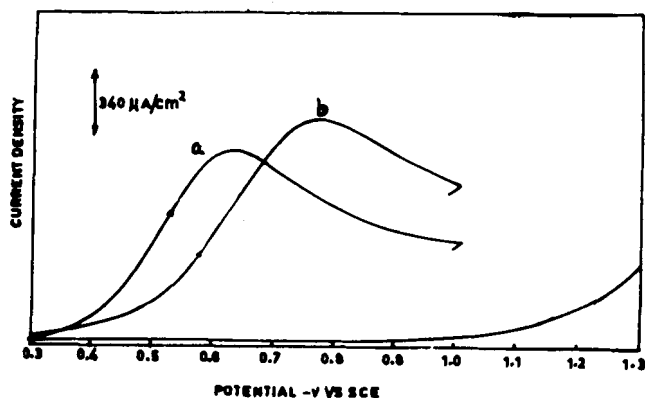
$$I_p = \frac{P}{Aer^{1/2}} = 2.98 \times 10^5 \times n(\propto n_a)^{1/2} D^{1/2} \quad ...(5)$$

In this equation, p is expressed in A, A in cm², C in mM, V in V.s⁻¹ and D is expressed in cm.² s⁻¹. Since $\propto n_a$ value is known from eq.(4) n the number of electrons involved and D the diffusion coefficient of the electroactive species are the only unknowns in these equations. From the polarographic investigations of nitrobenzene [17-18] and p-nitrophenol [19,20]
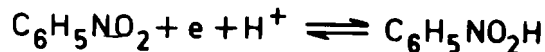
$$D_{NB} = 1.2 \times 10^{-5} cm^2 s^{-1} \quad and \quad D_{PNP} = 1.05 \times 10^{-5} cm^2 s^{-1}$$

may be assumed. With these values the n values of the nitrocompounds in the four different experimental conditions are tabulated (Table I).

Some important conclusions may be drawn from these investigations. Compared to Cu, the transfer coefficients on GC for both nitrobenzene and PNP are very much smaller. The actual cause for this behaviour is not clear at present. It may however be speculated that adsorption and blocking effects are more prevalent on GC electrode as compared to copper electrode.

As transfer coefficient decreases, the Ep should shift to more negative values [16] and the same is observed in the present case. Table I shows that the Ep value for the reduction of the same compound on GC is more negative than on Cu.

Compared to Hg [17-20] where both the compounds exhibit reversible charge transfer behaviour, the charge transfer on Cu as well as GC is much slower as evident from transfer coefficient measurements. However at sufficiently negative potentials the electrode processes on both the cathodes become diffusion controlled. This is evident from the fact that i$_p$ is proportional to $V^{1/2}$ and C in all the four sets of experiments. The n values calculated using eq.(5) show that n is 4 on both GC and Cu cathodes. Hence nitrobenzene undergoes a 4e reduction on both Cu and GC according to the following mechanism:

Fig. 3: L S V of PNP at G C electrode in 2M H₂SO₄ at a sweep rate of 40 mV.s⁻¹ at various concentrations of PNP(mM) (a)1, (b)1.5, (c) 2, (d) 2.5 and (e) 3.0

Fig. 4: L S V of nitrobenzene (a) and PNP (b) at G C electrode in 2M H₂SO₄ at a sweep rate of 40 mV.s⁻¹ and a concentration of 2 mM

$$C_6H_5NO_2 + e + H^+ \rightleftharpoons C_6H_5NO_2H$$
$$C_6H_5NO_2H + 3H^+ + 3e \longrightarrow C_6H_5NHOH + H_2O$$

The n value for PNP on GC is found to be 6 **(Table I)**. It is interesting to note that the actual peak current value of PNP on GC is only slightly higher than that of nitrobenzene as is evident from Fig.4. However taking note of the fact that D_{PNP} is less than D_{NB} and α_{na} of PNP is also less than α_{na} of NB, equation (5) clearly indicates that this should indeed be the case. Quantitative evaluations also support this view.

The n value of PNP on Cu is much lower than 6. PNP undergoes a 6e reduction in acid medium on Hg cathode because of the following chemical transformation [19,20]:
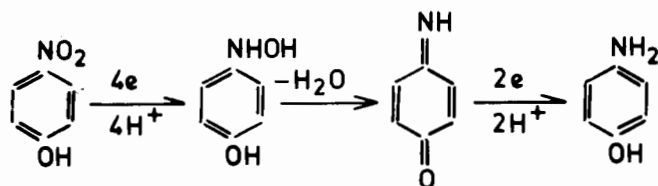
Since the quinonimine intermediate is more easily reducible than PNP itself the 6e wave is observed. The present work on GC also leads to the same result. In the preparative work with Cu cathode PNP as well as o-nitrophenol gives very good yields of the respective amino phenols [21,22]. Hence a low n value of 5.3 on Cu is quite perplexing. Pending any explanation, it may be assumed that this value is closer to 6 rather than 4 and hence PNP also undergoes a 6 electron transfer on Cu (since it is difficult to assume a 5e reduction process).

Although transfer coefficient values and Ep values are different, nitrobenzene and PNP undergo 4 and 6 electron reduction respectively on both Cu and GC cathodes. The main difference however is that the background reduction process occurs at different potential regions. Since H_2 evolution takes place very close to nitrobenzene reduction on Cu, both the processes are likely to occur simultaneously on Cu under the galvanostatic conditions employed in the preparative work. The nascent H_2 evolved on Cu cathode may reduce phenyl hydroxylamine to aniline.

Direct electroreduction of phenyl hydroxylamine on Cu (eq.3) may also take place along with H_2 evolution which cannot be deducted in the voltammetric curves.

Thus GC seems to be a better cathode as compared to Cu from the point of view of preparation of p-aminophenol from nitrobenzene. Since H_2 evolution requires about 700 mV of additional potential drop, in galvanostatic conditions the competition would be less pronounced. Voltammograms also suggest that phenylhydroxylamine is not directly reduced up to -1.25V.

CONCLUSION

The experiments indicate that nitrobenzene and PNP respectively undergo a 4e and 6e reduction on both Cu and GC cathodes.

However the hydrogen evolution reaction can be a parallel reaction on Cu cathode under galvanostatic conditions. Observation of improved yield of p-aminophenol on Cu cathode in presence of bismuth salts [8] may also be due to the increasing hydrogen overvoltage of Bi deposits. Hence carbon electrodes should prove to be a better choice for the electrochemical synthesis of p-aminophenol from nitrobenzene. Some preliminary preparative work carried out in this laboratory [23] also shows better yields on graphite as compared to Cu.

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