

ELECTROLYTIC PREPARATION OF QUINONE FROM BENZENE

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The electrolytic preparation of quinone from benzene is studied. The effects of various factors such as temperature, acid concentration of the electrolyte, current density on current efficiency have been tried and the results are presented. Temperatures ranging from 313-323K and low current densities favour oxidation. The results of the experiments carried out with lead dioxide deposited over titanium are compared with those obtained with lead dioxide formed on lead.

Key words: Electro-oxidation, quinone, lead dioxide anode

INTRODUCTION

Para-benzoquinone is a commercially important material to prepare hydroquinone, which is extensively used as photographic developer. It is used as tyre adhesive in rubber industry, antioxidant, monomer and inhibitor [1].

P-benzoquinone is commercially produced by chemical oxidation of aniline [2,3] with MnO_2 and sulphuric acid or with sodium dichromate. Though there are many patents for the vapour phase oxidation of benzene to quinone, none of them seems to be of any commercial feasibility.

The electrolytic preparation of p-benzoquinone has been reported [4-14], which involves oxidation of benzene in dilute sulphuric acid or a mixture of sulphuric acid and soluble sulphates at lead dioxide formed on lead anode. The patents differ from each other in the method of isolation of quinone and recirculation of the benzene. In the present study two types of lead dioxide anodes have been tried for the electrolytic preparation of quinone and various parameters influencing the current efficiency for the formation of quinone have been studied and the results are presented here.

EXPERIMENTAL

The cell consisted of a 2 litre beaker, fitted with a PVC cover having openings for the anode, diaphragm, stirrer, condenser and thermometer. An unglazed ceramic cylindrical porous pot was used as the diaphragm. The cathode was perforated lead sheet. Two types of lead dioxide anodes were employed. In one case, lead dioxide was formed on perforated lead (10.7 x 6.5 cm) and the same was used as anode.

In the second type, a titanium sheet (15 (h) x 10 cm (w)) covered with a thick layer of lead dioxide [15,16] was used. The cell in this case consisted of a glass trough with 18 cm dia, 10 cm height. 20% H_2SO_4 acid was used as the anolyte in the ratio of 3:1 for aqueous to organic phase. An auxiliary glass stirrer was employed for stirring the anolyte. Quinone formed was estimated volumetrically both in aqueous and organic phase and the percentage yield was calculated. Some amount of quinone floating on the surface was filtered, dried and taken into account for the calculation of current efficiency.

RESULTS AND DISCUSSION

It has been mentioned [17] that lead dioxide on graphite gives a better yield. Since the graphite is affected when the lead dioxide coating goes off, titanium substrate lead dioxide (TSLD) [15,16] is employed as anode and the results obtained with the same are compared with those obtained with the lead dioxide formed on lead.

Effect of acid concentration

Oxidation of benzene with both types of anodes were carried out at different H_2SO_4 concentrations. Examination of Table I shows that the current efficiency increases upto concentration of 20% and above this concentration, the current efficiency decreases. So 20% of H_2SO_4 is chosen as the optimum concentration of the electrolyte.

TABLE-I: Effect of acid concentration

Temperature = 318 to 323K; Current density = 0.25 $kA.m^{-2}$

No.	Acid concentration (%)	Current efficiency (%)	
		PbO ₂ on Pb	TSLD
1	5	30.3	35.6
2	10	32.6	38.8
3	20	40.4	52.8
4	25	31.3	36.7

Effect of temperature

The results of variation of current efficiency with of temperature (Table II) show that the current efficiency increases gradually upto 318-323K. Further increase in temperature affects the efficiency. This is observed for both types of electrodes.

TABLE-II Effect of temperature

Acid concentration 20%; current density 0.25 kA.m⁻²

No.	Temperature (K)	Current efficiency (%)	
		PbO ₂ on Pb	TSLD
1	298-303	29.5	30.5
2	308-313	33.0	38.7
3	318-323	40.4	52.8
4	328-333	34.4	37.2

Influence of current density

It is evident from Table III that lower current densities (0.25 kA.m⁻²) favour oxidation of benzene. The fall in current efficiency with increase in current density is due to the predominant oxygen evolution as it exceeds the limiting current density. The yield is also less due to further oxidation of quinone.

TABLE-III : Influence of current density

Temperature = 318-323K; Acid concentration = 20%

No.	Current density (kA.m ⁻²)	Current efficiency (%)	
		PbO ₂ on Pb	TSLD
1	0.12	30.4	37.5
2	0.25	40.4	52.8
3	0.37	27.8	35.0
4	0.50	22.4	28.7

Influence of duration of electrolysis:

Influence of duration of electrolysis on the efficiency of quinone formation with both types of electrodes is shown in TableIV. It is seen that increasing duration of electrolysis decreases the cur-

TABLE-IV: Influence of duration of electrolysis

Temperature = 318-323K; Current density: 0.25 kA.m⁻²
Acid concentration: 20%

No.	Duration (hrs)	Current efficiency (%)	
		PbO ₂ on Pb	TSLD
1	1	40.4	52.8
2	2	36.2	48.6
3	3	28.7	35.3
4	4	23.0	28.5

rent efficiency of quinone. It has already been reported [8] that if the concentration of quinone increases more than 1%, oxidation of quinone to oxalic acid cannot be avoided. Short durations of electrolysis only results in better oxidation efficiencies and continuation of electrolysis lowers quinone formation.

Anodic polarisation studies were made using SCE as the reference electrode (Fig.1). A displacement of up to 0.3V is observed,

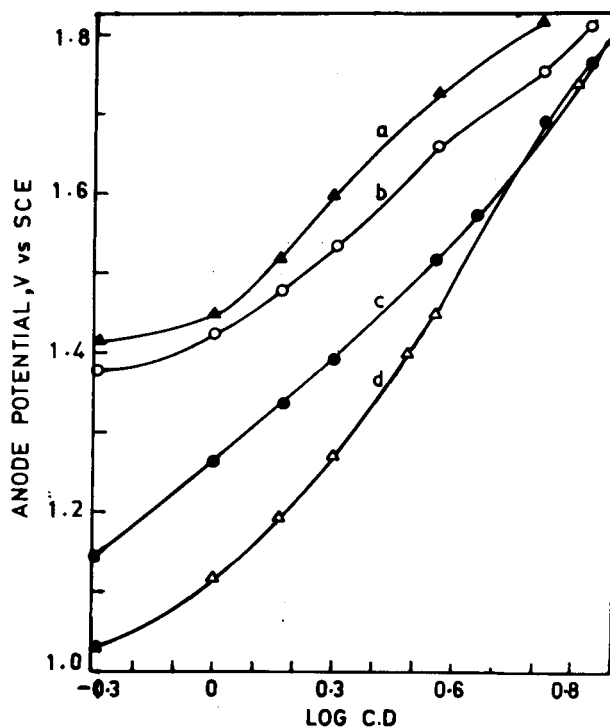


Fig.1: Variation of anode potential with current density (a) PbO₂ on Pb anode without depolariser, (b) TSLD anode without depolariser, (c) TSLD anode with depolariser, (d) PbO₂ on Pb anode with depolariser.

for PbO₂ on the Pb anode and 0.2V for TSLD anode at a current density 0.1kA.m⁻². The higher displacement may be due to the porous nature of the lead dioxide formed on lead surface which favours effective depolarisation [11].

Fig.2 shows the change of anode potential with duration for PbO₂ on Pb and TSLD anodes. It is seen that the anode potential in the case of TSLD (curve 1) remains constant whereas change is observed with time for lead dioxide on lead anode (curve 2). The lowering of the potential of PbO₂ formed on lead may be attributed to the porous nature of the deposit resulting in lowering of current density. The lowering of current efficiency for quinone formation in the same anode may be partly due to adsorption and oxidation of quinone.

From these studies it may be concluded that electrolytic oxidation of benzene to quinone can be carried out at TSLD anode with better efficiencies (52%) if carried out for shorter durations.

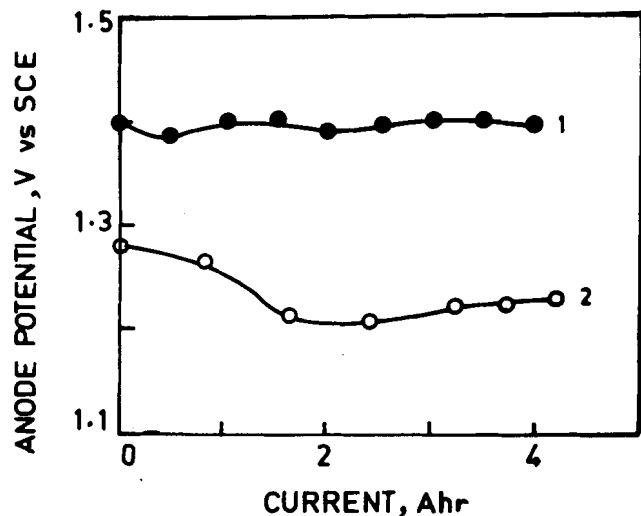


Fig.2: Variation of anode potential with quantity of electricity (a) TSLD anode, (b) PbO₂ on Pb anode

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