

PAIRED ELECTROCHEMICAL SYNTHESIS OF HYDROQUINONE FROM PHENOL

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In the present work, attempts have been made to prepare hydroquinone by paired electrochemical synthesis from phenol. Parameters such as temperature, electrolyte concentration, current density, electrode materials and its surface nature have been studied in an undivided cell. It is found that lead dioxide coated on Pb and Ti substrate acts as the best anode for the synthesis of hydroquinone.

Key words: Paired electrochemical synthesis, hydroquinone, lead dioxide coated electrodes

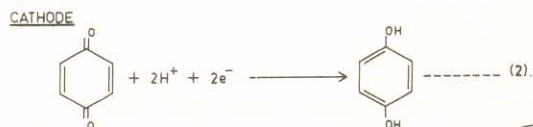
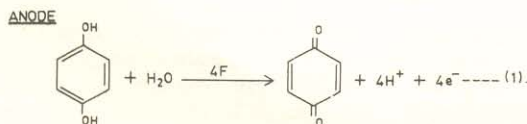
INTRODUCTION

Hydroquinone is mainly used as photographic developer in black and white photography and graphic arts. It is also used as tyre adhesives in rubber industry, anti-ozonants, antioxidants etc [1].

It is obtained by the chemical oxidation of aniline, hydroxylation of phenol or by the catalytic chemical oxidation of phenol [2]. It can also be prepared by the electrochemical oxidation of phenol to quinone at anode and subsequent reduction of quinone to hydroquinone at cathode [3-5]. In the present work, attempts have been made to get hydroquinone with higher efficiency by paired electrochemical synthesis from phenol. The effect of various parameters such as temperature, electrolyte concentration, electrode material and its surface nature have been studied in an undivided cell.

EXPERIMENTAL

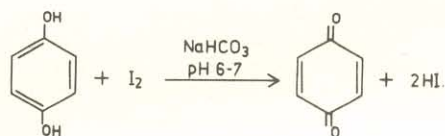
The electrolytic cell used for the oxidation of phenol consisted of a 500 ml beaker having a PVC lid with openings for electrodes and stirrer. The temperature was maintained by means of a water bath. When lead was used as anode material, pre-anodised lead with plain and texturised surface were tried. Cylindrical shaped lead was used to study the effect of rotation. Oxidations were also tried with lead dioxide on graphite and on titanium mesh. In a few experiments a divided cell was used resulting in the formation of quinone. In all these cases, dilute sulphuric acid was used as the electrolyte and lead was used as the cathode material. Reactions at the



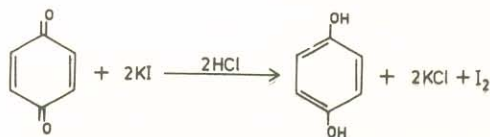
Theoretical amount of current was passed in all the cases.

Estimation

Hydroquinone formed was estimated using iodimetric method.



Unreduced quinone was also estimated iodometrically [6,7].



Unreacted phenol was estimated by bromometric method. For the completion of oxidation, the pH of the solution must be greater than 6.

Isolation of hydroquinone

After passing theoretical amount of current, the electrolyte was filtered to remove suspended impurities. 0.5g of solid sodium bisulphite was added to reduce residual quinone and the solution was saturated with sodium chloride. Then it was extracted with ether and ether was removed nearly to dryness. Cold carbon tetrachloride was added and hydroquinone precipitated as amorphous solid. The product was further purified by recrystallisation from water.

Identification of product

The melting point of the product and its acetyl derivative corresponded to that of hydroquinone (454K) and diacetate (397K) respectively. Cyclic voltammograms on HMDE were taken with standard solution and sample solution after electrolysis to identify the quinone in the solution.

RESULTS AND DISCUSSION

Effect of electrolyte concentration

Electrolytic oxidation was carried out in an undivided cell using lead cathode and freshly prepared surface of lead dioxide on lead as anode. Temperature was maintained between 323-328K and current density 5 A.dm⁻². A series of experiments were carried out with 3%, 5% and 7% (by weight) H₂SO₄ as electrolyte and the results are shown in Table I. It can be seen that as the acid concentration increases from 3% to 7%, the yield of hydroquinone decreases from 27% to 19%. This may be due to the formation of resinous products. In fact, it was found that under these conditions the anode surface was completely blocked by the resinous coating which hindered the oxidation of phenol thereby leading to a poor yield.

Effect of temperature

Studies on variation of temperature show (Table II) that maximum yield is obtained between 323-328K. Further increase in temperature resulted in a decrease in yield of hydroquinone. This may be due to the overvoltage effect.

Effect of current density

Different experiments were carried out at current densities varying from 5 to 20 A.dm⁻². It is clear from Table III that on further increase of current density the yield is found to be lowered. At current densities less than 10 A.dm⁻² the efficiency is low. This may be due to the re-oxidation of hydroquinone formed in preference to the oxidation of phenol. At current

densities higher than 10 A.dm⁻², the fall in efficiency may be due to the predominant oxygen evolution.

Effect of texturised lead electrodes

Electrolytic oxidations were carried out on prepolarised texturised electrodes at different apparent current densities from 7.5 to 15 A.dm⁻². It is evident from the results that the maximum yield of hydroquinone is obtained at an apparent current density of 10-12 A.dm⁻² and on further increase of current density, the yield of hydroquinone is found to be lowered. The increase may be attributed to the increase in ratio of p-benzoquinone to hydroquinone formed and the chemical efficiency of the process.

Effect of electrode materials

Electrolytic oxidation of phenol was carried out on platinum, freshly prepared lead dioxide on lead (both plain and texturised lead sheets) and lead dioxide coated on graphite and on titanium. Results showed that oxidation of phenol on PbO₂ deposited titanium and graphite gives better yield than PbO₂ on Pb. This shows that the nature of PbO₂ deposit plays an important role in the oxidation of phenol (Table IV).

Electrochemical oxidation of phenol carried out in a divided cell yields quinone. But the yield is low. This may be due to the blocking of electrode surface by benzoquinone formed. Passing of excess current also results in low yield. This may be due to further decomposition of product to dicarboxylic acids, carbon dioxide etc.

Effect of addition of inorganic salts during pre-anodization

Different inorganic salts of chromium-nickel and iron were used as addition agents during pre-anodising [8]. This pre-anodized, texturised electrodes are used for the oxidation of phenol in an undivided cell. Temperature was kept between 323-328K. From the results it is found that the yield of hydroquinone is not increased by the addition of inorganic salts during pre-anodizing.

TABLE I: Effect of acid concentration on the preparation of hydroquinone

Anode: Freshly prepared PbO₂ on Pb, Anode area: 0.39 dm², Current density: 5 A.dm⁻², Cathode: Lead, Temperature: 313-318K, Electrolyte: 3% H₂SO₄ (300 ml), Volume of phenol: 9 ml, Quantity of current passed: 10 A.hr

Expt. No.	H ₂ SO ₄ concentration (weight %)	Cell voltage (V)	Hydroquinone (gm)	Quinone (gm)	Unreacted phenol (gm)	Yield (%)
1	3	4.5	2.3	0.14	0.20	27.5
2	5	5.0	1.8	0.08	0.30	21.0
3	7	7.0	1.5	0.08	0.52	19.4

TABLE II: Effect of temperature on the preparation of hydroquinone

Anode: Freshly prepared PbO₂ on Pb, Electrode area: 0.39 dm², Current density: 10 A.dm², Cathode: lead, Quantity of current passed: 10 A.hr. Electrolyte: 3% H₂SO₄ (300 ml), Volume of phenol: 0.9 gm

No.	Temperature (K)	Cell voltage (V)	Hydroquinone (g)	Quinone (g)	Unreacted phenol (g)	Yield of hydroquinone (%)
1	303-308	6.1	2.65	0.15	0.60	31
2	313-318	6.3	2.82	0.14	0.53	33
3	323-328	6.5	3.08	0.12	0.48	36
4	328-333	6.6	2.26	0.10	0.61	27

TABLE III: Effect of current density on the preparation of hydroquinoneAnode: Freshly prepared PbO₂ on Pb, Cathode: Lead, Temperature: 323–328K, Quantity of current passed: 10 A.hr, Electrolyte: 3% H₂SO₄ (300 ml), Volume of phenol: 9.0 gm

No.	Current density (A.dm ⁻²)	Cell voltage (V)	Hydroquinone (g)	Quinone (g)	Unreacted phenol (g)	Yield of hydroquinone (%)
1	5.0	4.5	2.3	0.20	0.14	27.5
2	7.5	4.7	2.5	0.20	0.80	33.0
3	10.0	5.5	2.82	0.14	0.50	36.0
4	12.5	6.2	2.7	0.16	0.31	32.0
5	15.0	6.7	2.6	0.20	0.30	28.0
6	17.5	8.3	1.9	0.20	0.24	25.0
7	20.0	8.6	1.8	0.25	0.20	22.0

TABLE IV: Effect of electrode materials on the preparation of hydroquinoneCathode: Lead, Anode current density: 10 A.dm⁻², Temperature: 323–328, Amount of current passed: 10 A.hr, Electrolyte: 3% H₂SO₄ (300 ml), Volume of phenol: 9 ml

No.	Anodes	Cell voltage (V)	Hydroquinone (g)	Quinone (g)	Unreacted phenol (g)	Yield of hydroquinone (%)
1.	Platinum	6.2	0.56	0.03	7.90	6
2.	Freshly prepared PbO ₂ on Pb	5.5	2.81	0.14	0.53	33
3.	Freshly prepared PbO ₂ on texturised lead	6.0	3.20	0.24	0.42	39
4.	PbO ₂ coated on Ti	5.6	4.02	0.29	0.34	48
5.	PbO ₂ coated on graphite	5.4	3.90	0.28	0.35	46.5

Anodic polarization study

Anodic potential measurements are taken for the oxidation of phenol on freshly prepared lead dioxide on lead at 313K and 333K (Fig. 1). It is not possible to get a clear idea about the role of electrode potential on the oxidation of phenol. The catalytic nature of oxide electrode surface and its irreproducible behaviour may be the reason for not being able to give a satisfactory explanation of these studies. Prevailing opinion is that whatever may be the anode material, the oxidation of aromatic hydrocarbons and their hydroxyl radicals follows the ECE mechanism [9]. From the experimental data, it can be confirmed that oxidation of phenol gives better yield on lead dioxide anode within the range of anodic water decomposition potentials.

CONCLUSION

From these studies it can be concluded that phenol can be electrochemically oxidised to hydroquinone in 3% H₂SO₄ medium with the efficiency of 50% at lead dioxide on titanium or graphite substrate anodes at higher current densities (10–12.5 A.dm⁻²) in an undivided cell.

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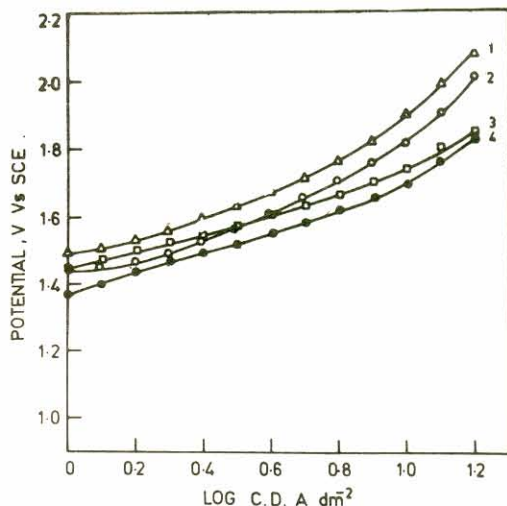


Fig. 1: Anodic (Pb) polarisation study

- (1) H₂SO₄; 313 K (2) H₂SO₄ + C₆H₅OH; 313 K
- (3) H₂SO₄; 333 K (4) H₂SO₄ + C₆H₅OH; 333 K

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