JOURNAL OF APPLIED ELECTROCHEMISTRY **19** (1989) · SHORT COMMUNICATION

SHORT COMMUNICATION

Oxidation of phenol to benzoquinone in a CSTER with modulated alternating voltage

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Received 24 November 1988; accepted 29 December 1988

1. Introduction

Recently, it has been shown that the low selectivity and slowness in the electrokinetics of electroorganic reactions can be improved by electrolysis using modulated alternating current (a.c.) or alternating voltage (a.v.). The method has the advantages that: (i) no catalysts are needed; (ii) no cell modification is required; and (iii) no electrolyte additives are needed, thus avoiding the possible contamination of reaction products. The detailed literature review on the effects of a.c. and a.v. on electroorganic reactions is given in [1–4].

This paper is concerned with a study of improving the rate of *p*-benzoquinone production using modulated sinusoidal a.v. *p*-Benzoquinone is obtained by electrooxidation of phenol in a divided cell [5]:

$$C_6H_5OH + H_2O \; = \; C_6H_4O_2 + 4H^+ + 4e^- \quad (1)$$

In an undivided cell, the *p*-benzoquinone produced at the anode is further reduced to hydroquinone at the cathode and no net *p*-benzoquinone is produced in the overall process. Platinum, graphite and lead dioxide have been used as the electrodes, and aqueous sulfuric acid in the concentration range of 3–20 wt % is used as the supporting electrolyte. *p*-Benzoquinone is used in photographic processing, manufacture of dyes, manufacture of hydroquinone, tanning of leathers and as an oxidizing reagent for laboratory applications.

The use of a.v. to enhance the conversion of phenol to hydroquinone in an undivided batch electrochemical cell was described earlier [1]. In the present study, a continuous stirred tank electrochemical reactor (CSTER), whose anode compartment is separated from the cathode compartment with a cell separator, is used to oxidize phenol to *p*-benzoquinone. This paper describes the experimental results of the effect of modulated sinusoidal a.v. on the reaction rate, the yield of *p*-benzoquinone and the energy requirements of the continuous electrooxidation process.

2. Experimental details

An a.v. modulation technique was used in the present investigation. In this technique, a constant sinusoidal a.v. of known magnitude and frequency was superimposed onto a d.c. potential by feeding the a.v. signal from a function generator (Hewlett Packard 3311A) to a potentiostat (Wenking HP 72). The resulting composite potential wave (a.v. plus d.c. potential) was then applied between the working and reference electrodes of an electrochemical cell. A digital data acquisition system consisting of a data logger (Hewlett Packard 3421A), a microcomputer (Commodore PET 4032), a disk drive (Commodore 4040) and a line printer (Commodore 4022), was used to measure the d.c. current, root mean square (RMS) of a.c. current, d.c. cell voltage, and RMS of a.c. cell voltage as functions of applied d.c. potential and modulated a.v. The details of electric circuit and experimental technique have been described [2, 6, 7] and will not be repeated here.

2.1. *Cell setup and electrolytes*

A three-compartment H-type glass cell (Electrosynthesis C-200) was used in the present investigation. The working electrode compartment had a capacity of 175 ml; it was separated from the counter electrode and 1 M sulfuric acid (pH 0.6). The electrolytes in the counter electrode and reference electrode compart-the counter electrode, and a saturated calomel electrode (SCE) served as the reference electrode.

The electrolyte in the working electrolyte compartment was an aqueous solution of 0.05–0.1 M phenol and 1 M sulfuric acid (pH 0.6). The electrolytes in the counter electrode and reference electrode compartments were 1 M sulfuric acid (pH 0.6). The electrolyte temperature was maintained at 25 ± 2° C throughout this study.

2.2. *Polarization measurements*

A platinum rotating disk electrode (Pine Instrument DT6), having an exposed area of $0.458\,cm^2$ was used to examine the effect of modulated 60 Hz sinusoidal a.v. on the d.c. current vs d.c. potential relations for the oxidation of phenol to benzoquinone. For each run, the platinum disk electrode was electrolytically cleaned in 1 M NaOH, transferred to the working electrode compartment of the cell and installed on a rotator (Pine Instrument ASR2). A constant sinusoidal a.v. of known magnitude was applied between the platinum disk and reference electrodes from the a.v. modulation circuit. The d.c. potential was swept between 0 and 1.5 V vs SCE at a rate of $0.005\,V\,s^{-1}$. The resulting d.c. current from the cell was recorded

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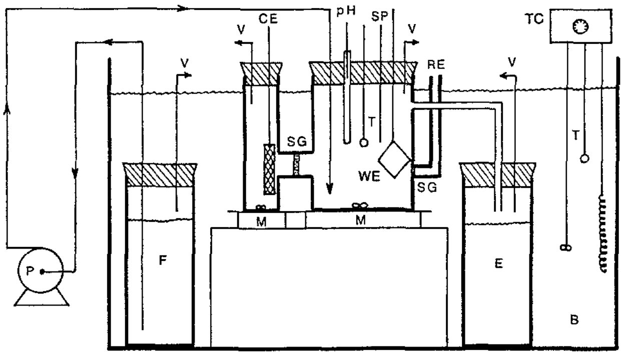

Fig. 1. Schematic diagram of the CSTER setup. B, constant temperature water bath; CE, counter electrode; E, exit electrolyte reservoir; F, feed electrolyte reservoir; M, magnetic stirrer; P, pump; pH, pH electrode; RE, reference electrode; SG, sintered glass cell separator; SP, electrolyte sampling port; T, thermometer; TC, temperature controller; V, vent; WE, working electrode.

as a function of d.c. potential under the modulated a.v. conditions.

2.3. *Potentiostatic CSTER experiments*

The working electrode compartment of the H-type glass cell was operated as a continuous stirred tank electrochemical reactor (CSTER) to oxidize phenol to *p*-benzoquinone with modulated sinusoidal a.v. A schematic of the cell arrangement and flow equipment is shown in Fig. 1. A metering pump (Liquid Metronics A101-95T) was used to pump the phenol and sulfuric acid electrolyte from a feed solution reservoir to the inlet port of the working electrode compartment. An electolyte overflow port fused to the side of the working electrode compartment was used to discharge the product stream to a product solution reservoir. Dilute sulfuric acid (1 M) having the same pH as that of the anolyte was used in the counterelectrode and reference electrode compartments. The entire cell assembly, feed and product solution reservoirs were immersed in a constant temperature water bath as shown in Fig. 1.

A stationary platinum foil of 12.9 cm^2 surface area was used as the working electrode for the continuous electrolysis experiments. For each run, the working electrode was mechanically polished to 600-grit smoothness, and electrolytically cleaned in 1 M NaOH. The cell was assembled and the feed solution reservoir was charged with a freshly prepared electrolyte of known phenol concentration. The electrolyte was pumped into the working electrolyte compartment and the electrolytes in both the working electrode and counter electrode compartments were magnetically stirred to ensure a uniform concentration in each compartment. A d.c. potential superimposed with 60 Hz sinusoidal a.v. of known magnitude was applied between the working and reference electrodes. The d.c. current, RMS a.c. current, d.c. cell voltage, and RMS a.c. cell voltage were recorded with the digital data acquisition system. The electrolysis was continued until a steady state was reached (approximately 5–6 h). A 5-ml solution sample was withdrawn from the working electrode compartment at periodic intervals. The concentration of phenol was determined using a bromination and iodometric titration method. A polarographic technique using a dropping mercury electrode (DME) was used to analyze *p*-benzoquinone. The *p*-benzoquinone concentration was determined by measuring the limiting current for the reduction of *p*-benzoquinone to hydroquinone on the DME, and by comparing the magnitude of the limiting current to a calibration curve. The details of the chemical analysis procedures are described in [8].

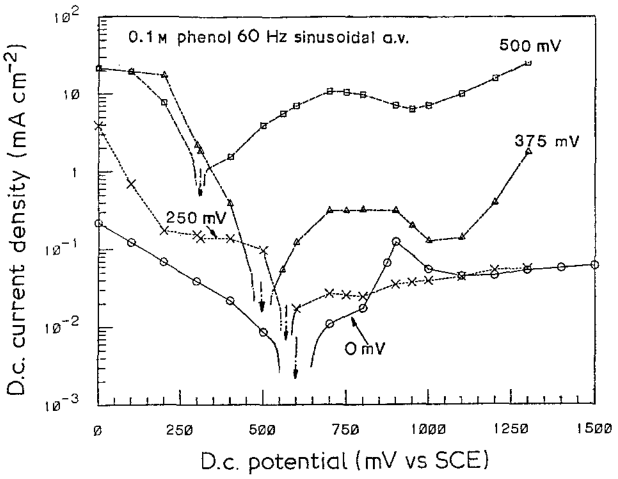

Fig. 2. D.c. polarization curves with modulated 60 Hz sinusoidal a.v. for platinum in 0.1 M phenol and 1 M sulfuric acid. A platinum rotating disk electrode at 2400 rpm was used for the measurements.

3. Results and discussion

3.1. *Polarization measurements*

The polarization curves for the oxidation of phenol to *p*-benzoquinone with modulated 60 Hz sinusoidal a.v. were measured over the a.v. magnitude of 0–500 mV RMS and electrode rotational speed of 600–2400 rpm. It was found that the rotational speed of the platinum disk electrode had no significant effect on the polarization measurements, and all the data were collected at a rotational speed of 2400 rpm.

The typical d.c. current vs d.c. potential polarization curves of platinum in 0.1 M phenol and 1 M sulfuric acid with 60 Hz sinusoidal a.v. are given in Fig. 2. The arrows in the figure indicate the location of the rest potentials where the d.c. current passing across the electrode surface was zero. The anodic curves were for the oxidation of phenol to *p*-benzoquinone, and the cathodic curves corresponded to the reduction of dissolved oxygen on platinum. The anodic curve without a.v. exhibited a current peak at the d.c. potential of 0.9 V vs SCE. The current peak was caused by the adsorption of the oxidation products on the electrode surface. The adsorbed film caused the d.c. current to decrease with further increase in d.c. potential. Application of a.v. greater than 250 mV RMS shifted the rest potential toward the negative direction and significantly increased the d.c. current for the oxidation of phenol to *p*-benzoquinone. With 500 mV RMS a.v. the anodic d.c. current was more than two orders of magnitude greater than that without

Table 1. Results of steady-state CSTER experiments for the oxidation of phenol to p-benzoquinone

Modulated sinusoidal a.v. (mV, RMS)	*Cell current*		*Anode–cathode cell voltage*		*Exit electrolyte concentration* (M)		*Conversion of phenol* (%)	*Yield of p-benzoquinone* (%)	*Electric energy per mole of p-benzoquinone* (J mol^{-1})
	D.c. (mA)	*A.c.* (mA, RMS)	*D.c.* (V)	*A.c.* (V, RMS)	*Phenol*	*p-Benzoquinone*			
0	0.13	0	0.95	0	5.00×10^{-2}	0	0	–	–
250	10	40	1.9	0.45	4.93×10^{-2}	0.15×10^{-3}	3.2	9.3	0.4×10^{8}
500	270	390	4.5	4.3	4.43×10^{-2}	2.38×10^{-3}	12.9	36.2	1.8×10^{8}
750	660	910	5.7	5.9	3.16×10^{-2}	8.00×10^{-3}	36.9	43.3	1.6×10^{8}

Anode: platinum with 12.9 cm^2 surface area; d.c. potential of anode: 1.5 V vs SCE; volume of anode compartment: 175 ml; concentration of phenol in feed electrolyte: 0.05 M; volummetric flow rate of feed electrolyte: 25 ml h^{-1}; cell temperature: 25 ± 2° C.

a.v. This increase in the d.c. current was partly due to the enhancement of apparent reaction kinetics and partly due to the removal of the adsorbed film by the modulated a.v. as explained in [6–8].

3.2. *Results with CSTER*

In the CSTER experiments, the d.c. potential of the platinum working electrode was controlled at 1.5 V vs SCE. Sixty Hz sinusoidal a.v. of 0–750 mV RMS magnitude was modulated onto the d.c. potential. These conditions were chosen from the results of the polarization measurements. The working electrode compartment was continuously fed with an electrolyte containing 0.05 M phenol and 1 M sulfuric acid at a rate of 25 ml h^{-1}. Samples of the exit electrolyte were analyzed to determine the concentrations of phenol and *p*-benzoquinone. From the steady-state concentration values, the conversion of phenol and yield of *p*-benzoquinone were calculated from the following equations:

$$X(\text{conversion}) = (C_{\text{P,feed}} - C_{\text{P,exit}})/C_{\text{P,feed}} \qquad (2)$$

$$Y(\text{yield}) = C_{\text{B,exit}}/(C_{\text{P,feed}} - C_{\text{P,exit}}) \qquad (3)$$

where $C_{\text{P,feed}}$ is the concentration of phenol in the feed electrolyte; and $C_{\text{P,exit}}$ and $C_{\text{B,exit}}$ are the steady-state concentrations of phenol and *p*-benzoquinone in the exit electrolyte, respectively.

Table 1 summarizes the steady-state results of the CSTER experiments at four modulated a.v. magnitudes of 0, 250, 500 and 750 mV RMS. It is seen that the d.c. current passing through the cell increased with increasing magnitude of modulated sinusoidal a.v. With 750 mV RMS a.v., the d.c. current was 6000 times greater than that without a.v. The results indicate that modulated a.v. enhanced the reaction rate and the conversion of phenol in the CSTER. Without a.v., the conversion of phenol was nearly zero and no *p*-benzoquinone was produced at the d.c. anode potential of 1.5 V vs SCE. With the modulated a.v., both the conversion and yield were increased. At 750 mV RMS a.v., the conversion of phenol was increased to 37%, and the yield of *p*-benzoquinone was increased to 43%.

The required electric energy per mole of *p*-benzoquinone produced is given in the last column of Table 1. The values were calculated from the cell current and cell voltage data using the relation:

$$W = (E_{\text{dc}} I_{\text{dc}} + E_{\text{ac}} I_{\text{ac}})/(V C_{\text{B,exit}}) \qquad (4)$$

where W is total electric energy per mole of *p*-benzoquinone produced, E_{dc} and I_{dc} are the steady-state d.c. cell voltage and d.c. current during the electrolysis, E_{ac} and I_{ac} are the steady-state RMS a.c. cell voltage and RMS a.c. current, V is the volumetric flow rate of the electrolyte to the CSTER and $C_{\text{B,exit}}$ is the *p*-benzoquinone concentration in the exit electrolyte. The results indicate that the energy requirement per mole of *p*-benzoquinone product increased with increasing magnitude of modulated a.v. This was due to the fact that a large amount of electric energy was consumed by the a.c. cell voltage and a.c. current during the electrolysis. It should be noted that the energy values reported in Table 1 were accurate only for the present cell configuration. In an industrial electrolyzer, the energy requirement can be reduced by increasing the area of cell separator and by reducing the anode–cathode distance to decrease the ohmic potential drop in the cell.

4. Conclusions

The modulated a.v. enhanced the d.c. current for the oxidation reaction, and shifted the rest potential in the negative dirrection. A.v. increased the rate of conversion of phenol and improved the yield of *p*-benzoquinone. Without a.v., no *p*-benzoquinone was produced in the potentiostatic d.c. electrolysis. With modulated 60 Hz sinusoidal a.v. of 750 mV RMS, the yield of *p*-benzoquinone was increased to 43%. The specific energy consumption increased with increasing magnitude of the modulated a.v.

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