Electrochemical oxidation of benzene at a glassy carbon electrode

K.-W. KIM[1], M. KUPPUSWAMY[2] and R.F. SAVINELL[2]*
[1]*Korea Atomic Energy Research Institute, Yusong PO Box 105, Taejeon 305-600, Korea;*
[2]*Ernest B. Yeager Center for Electrochemical Sciences and Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106, USA*
*(*author for correspondence)*

Abstract

Benzene oxidation in sulfuric acid at a glassy carbon electrode was investigated using voltammetric, chronoamperometric, and spectroscopic methods. The results are compared with those at a Pt electrode. Benzene was observed to be oxidized to benzoquinone presumably by active oxygen that was adsorbed on the GC electrode in the oxygen evolution region. It is concluded that oxidation at glassy carbon can produce benzoquinone or quinone-like compounds from an aqueous benzene solution. The applied potential for benzene oxidation should be less than 2.1 V vs RHE in order to prevent glassy carbon electrode damage by oxidation during long operation.

1. Introduction

The anodic oxidation of benzene is of environmental interest because its study could be a model case for the removal of the volatile carcinogenic compounds of BTX (benzene, toluene, and xylene) from contaminated waters [1]. In addition, direct electrochemical oxidation of benzene could lead to the manufacture of useful organic compounds such as benzoquinone, which can be reduced easily to hydroquinone, thus providing an antioxidant for the manufacture of rubber and other products. Other major products from benzene oxidation are maleic acid and carbon dioxide [2]. Complete oxidation of benzene to CO_2 by mediated electrochemical oxidation (MEO) through Ag^{2+} ions has been shown to be effective [3]. MEO of benzene also has the advantage that the homogeneous reaction is not limited by low concentrations of the substrate. However, direct electrochemical oxidation may be more amendable to partial oxidation to yield valuable biproducts. Direct oxidation of benzene in a fuel cell also has the possibility of cogenerating electricity [4, 5].

For the study of benzene direct electrochemical oxidation, several kinds of metal and metal oxide electrodes could be selected [6]. In particular, a lead oxide electrode is known to be most effective for oxidation of organic compounds [7, 8]. However, dissolution of lead into the treated solution, which results in the need for further treatment after the electrochemical process, is a significant problem. In the case of a glassy carbon (GC) electrode, its corrosion products are simply carbon dioxide and carbon particles, which are nontoxic and environmentally friendly (or inert). The carbon elec-

trode is known to be less effective than lead oxide but better than nickel or platinum toward benzene oxidation [8]. Moreover, a fine fibre type of glassy carbon is available, a column of which could be easily used to manufacture a flow-through electrolytic system with an extremely large electrode area for high throughput and cost-effective operation [9, 10].

The amount of literature relating to the anodic oxidation of aromatic organic compounds, especially benzene, at a GC electrode is scant as compared to the amount of literature on aliphatic compounds. Some authors have studied and measured the amounts of the organic compounds oxidized directly in a two-electrode system rather than observing the electrochemical behavior of the species at electrodes in detail [4, 7, 8]. In this work, voltammograms and chronoamperograms of background electrolyte and benzene-containing electrolyte at a GC electrode were measured and compared to those at a Pt electrode. Following electrolysis in a benzene-containing electrolyte, products in the electrolyte were directly analysed by u.v. and gas chromatography/mass spectroscopy. A probable mechanism of the benzene oxidation at a GC electrode is suggested.

2. Experimental details

The electrochemical cell was constructed from a 250 ml jacketed glass beaker (Lab Glass) fitted with a Teflon top with holes for inserting the electrodes and a gas bubbler. Glassy carbon and platinum (Pine Instruments) were used as working electrodes (geometric area 0.4558 cm^2). A platinum wire was used as the counter

electrode and a reversible hydrogen electrode (RHE) was used as the reference electrode.

Solutions were prepared with water that was doubly distilled and deionized (Ultrapure, Millipore). Benzene and H_2SO_4 (Fisher Scientific) were used as received without further treatment. The concentration of H_2SO_4 in the electrolyte was fixed at 0.5 M. Experiments were performed at 23 ± 0.5 °C. All the tests were carried out in an oxygen-free atmosphere by purging electrolyte solution vigorously with pure argon gas for 10 min. Before every run, the working electrode was pretreated by first polishing with 0.05 μm gamma alumina (Buehler), cleaning in a sonicator for 15 min, then washing with ultrapure water. Finally, the electrode was electrochemically cleaned at a scan rate of 100 mV s^{-1} for 20 min between 0.04 and 2.1 V vs RHE. A platinum working electrode of the same area as that of the GC electrode was used to compare directly the current for benzene oxidation. The products following electrolysis at 2.1 V vs RHE, for about 5 h in benzene-containing electrolyte, were directly analysed by a spectrophotometer (UV-160A, Shimadzu) and a gas chromatograph with double focusing mass spectroscopy (Donan 6000 series/SX-102A Jeol).

3. Results and discussion

Figure 1 shows cyclic voltammograms for background electrolyte and for benzene-containing electrolyte at a GC electrode for several different potential ranges. With benzene present, anodic and cathodic peaks around 0.7 V vs RHE were observed, and the magnitude of these peaks depended on the maximum positive potential scanned. When the upper potential limit is low, such as 1.6 V at which no oxygen evolution takes place, no peaks are seen around 0.7 V. As the upper limit of the potential range becomes more positive so that the oxygen evolution commences, the anodic and cathodic peaks around 0.7 V become more distinct and larger. Also, a significant difference in currents between benzene-containing and background electrolytes at potentials in the oxygen evolution region such as between 2.0 and 2.2 V is observed as shown in the small box in Figure 1.

There is no difference in current between benzene-containing and background electrolyte when the maximum applied potential is below 1.6 V. This result suggests that the benzene oxidation must depend on events occurring in the oxygen evolution region. Papers published recently on the pretreatment of several carbon electrodes show that the surface of a graphite anode under high polarization, corresponding to noticeable gas evolution, is appreciably covered by oxygen in the form of surface oxides or active oxygen [11–17]. This adsorbed oxygen is known to be very active and the rate of adsorption of oxygen on the surface does not depend on pH. Also, the nature and amount of the adsorbed active oxygen is found to depend highly on the potential. Yamanaka et al. and others suggested that hydroqui-
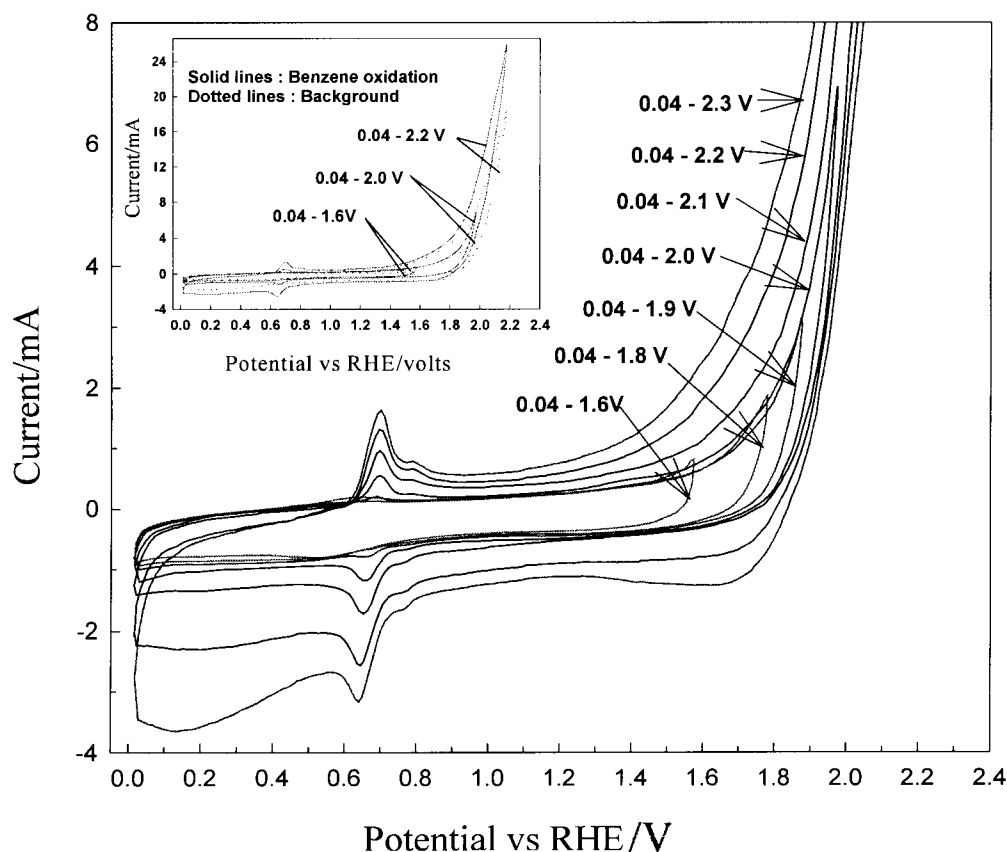

Fig. 1. Effect of maximum potential applied for benzene oxidation at a GC electrode. (Scan rate 100 mV s^{-1}).

none is generated from oxidation of benzene by this active oxygen [4, 5, 14, 16]. Based on literature reports, the anodic and cathodic peaks observed at about 0.7 V vs RHE are supposed to be due to oxidation of hydroquinone and reduction of benzoquinone, respectively [4, 5, 18], which is a two-electron process:

$$C_6H_4O_2 + 2\,H^+ + 2\,e^- \rightleftharpoons C_6H_4(OH)_2$$
$$E^\circ = 0.6992\,\text{V vs SHE} \tag{1}$$
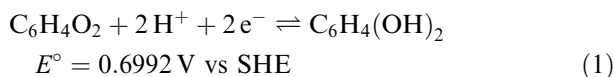
The standard potential for Equation 1 agrees well with the potential of anodic peaks in Figure 1.

Figure 2 shows the voltammograms for benzene oxidation at a GC electrode during different cycles. This result confirms indirectly the benzene oxidation mechanism shown above. No peak is observed in the anodic scan of the first cycle, but a peak appears in the cathodic scan of the first cycle after passing through the oxygen evolution region. A peak begins to appear at 0.7 V in the second anodic scan, after which the anodic and cathodic peaks appear to become stable. There is about a 3 mA difference between the benzene oxidation current and the background current at 0.7 V. The fact that the peaks in the anodic scan exist around 0.7 V starting with the second cycle (instead of the first cycle) must mean that the peak is not due to direct benzene oxidation at that potential but due to oxidation of hydroquinone which results from the reduction of benzoquinone generated in the oxygen evolution region. Accordingly, on the basis of these results and other related results [4, 5, 15, 16], a probable oxidation mechanism for benzene at a GC electrode could be as follows. First, oxygen evolution occurs at the GC electrode (Equation 2) and the oxygen is adsorbed at the electrode as an activated intermediate species (Equation 3). This adsorbed oxygen is then involved in the benzene oxidation reaction (Equation 4) to generate benzoquinone. The overall reaction is expressed in Equation 5.

$$2H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \tag{2}$$

$$O_2 \rightarrow 2\,O^*_{\text{Ads,surface}} \tag{3}$$

$$2\,O^*_{\text{Ads,surface}} + C_6H_6 \rightarrow C_6H_4O_2 + 2\,H^+ + 2\,e^- \tag{4}$$

$$2\,H_2O + C_6H_6 \rightarrow C_6H_4O_2 + 6\,H^+ + 6\,e^- \tag{5}$$

Voltammograms for benzene oxidation and the background were measured at different rotation speeds of the GC electrode. The peaks of anodic and cathodic scans at 0.7 V for a stationary GC electrode were observed to be a little larger than those for a rotating electrode. Moreover, no noticeable change was observed between the stationary and rotating electrodes in the voltammograms for the background electrolyte and for the benzene-containing electrolyte. This could be explained by benzoquinone and hydroquinone on the electrode being dissipated as the electrode is rotated so that the surface concentrations become low, thus resulting in low peak currents. If these peaks were due to the direct benzene oxidation at the electrode, then the peaks should increase with the rotation rate (in the case of a mass transfer-controlled reaction), or they should remain constant with the rotation speed (in the case of the charge-transfer controlled reaction).

Figure 3 shows the effect of scan rate on benzene oxidation. The current for the benzene-containing electrolyte increases with an increase in scan rate. The peaks for oxidation of hydroquinone become much more defined and larger. The peak current, as shown in the inset box, is observed to be linear with the square root of scan rate and the anodic peak potential shifts only a little in the positive direction with the scan rate. Thus, it appears that the redox reaction represented by Equation 1 behaves nearly reversibly. The anodic and cathodic peak charges (corrected for charging currents) at 200 mV s^{-1} were calculated to be approximately 2.0×10^{-3} and 2.2×10^{-3} C, respectively. For the same scan rate, the net charge for the benzene oxidation reaction was estimated after subtraction of the background current in the range from 1.6 to 2.1 V (the region where benzene oxidation occurs) to be approximately 2.1×10^{-3} C. These near equivalent charges again
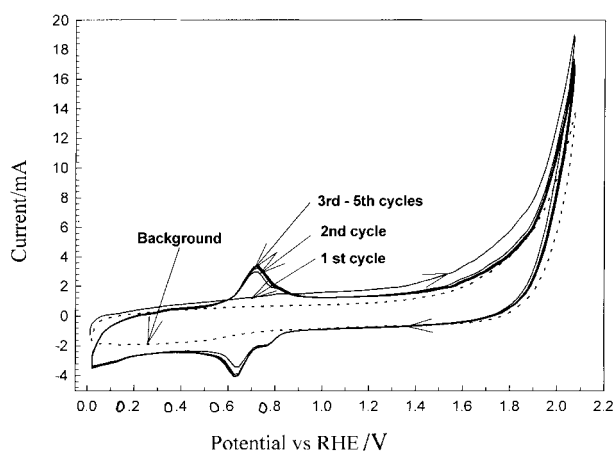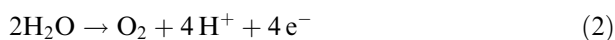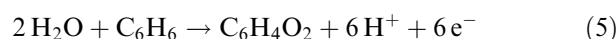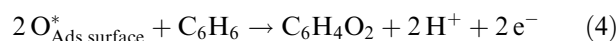

Fig. 2. Cyclic voltammograms for benzene-containing electrolyte at a GC electrode at different cycles. (Scan rate 200 mV s^{-1}).
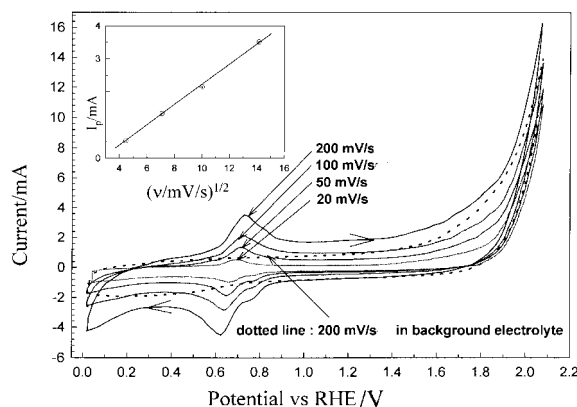

Fig. 3. Cyclic voltammograms for benzene-containing and background electrolytes at a GC electrode at different scan rates.

suggests that benzoquinone is generated by the oxidation of benzene through some form of active oxygen [17].

Figure 4 shows chronoamperograms for benzene-containing and background electrolytes at the GC electrode at several applied potentials. At first, the currents decrease rapidly because of the charging current. After that, the currents approach values that are time-independent. Similar to the results in Figure 1, time-independent values at low applied potentials, for example, 1.6 and 1.8 V, are close to zero. However, at higher applied potentials where the oxygen evolution occurs noticeably as seen in Figure 1, there was a significant difference in the time-independent current values between benzene-containing and background electrolytes. In this experiment, the chronoamperograms at different rotation speeds, (900, 1,600 and 2,400 rpm) were carried out, but no difference was observed in the currents. This suggests that the benzene oxidation step, Equation 4, is charge-transfer controlled. The chronoamperometry measurement could not be carried out at a stationary electrode because many tiny gas bubbles evolved at the potential where the benzene oxidation takes place, which resulted in large current fluctuations, or even a completely gas-covered electrode.

Figure 5 shows the net oxidation current of benzene estimated from the results in Figure 4 after 400 s as a function of applied potential. There is no net benzene oxidation current until 1.6 V. However, beyond 1.6 V, the benzene oxidation current increases rapidly and shows a peak at 2.1 V. The increase of benzene oxidation current with the applied potential is again consistent with the increase in the amount of activated oxygen adsorbed on the GC electrode. Beyond a potential of 2.3 V, the net benzene oxidation current could not be determined because currents were observed to decrease rapidly and irregularly. Moreover, scratches and grooves were observed to appear on the electrode surface after the experiment. We suspect that these observations are related to damage of the GC electrode due to corrosion processes at high potentials. However,

Fig. 5. Net benzene oxidation current vs applied potential.

there was no damage on the electrode visually observed after the electrode was used for about 500 s below 2.1 V, and the electrode surface was still as shiny as it was just immediately after polishing. The corrosion processes at a GC electrode at high anodic potentials was examined and elucidated by Gattrell et al. [7] who studied phenol oxidation at a GC electrode in a two-electrode system. They found that a high electrode resistance, formed by products of the electrode surface corrosion, made the actual electrode potential lower than the applied potential. Therefore, we suspect that the decrease in oxidation current of benzene at potentials beyond 2.3 V could be attributed to electrode corrosion processes. In view of this result, a suitable applied potential for the benzene oxidation at a GC electrode should be less than 2.1 V.

To confirm the product identification of benzene oxidation at a GC electrode, an electrolysis at 2.1 V vs RHE in benzene-containing electrolyte was carried out for about 5 h with the GC electrode of 0.46 cm^2 area in the undivided cell. Then, a cyclic voltammogram at a freshly prepared GC electrode was recorded in the solution; the result is shown in Figure 6. The volta-
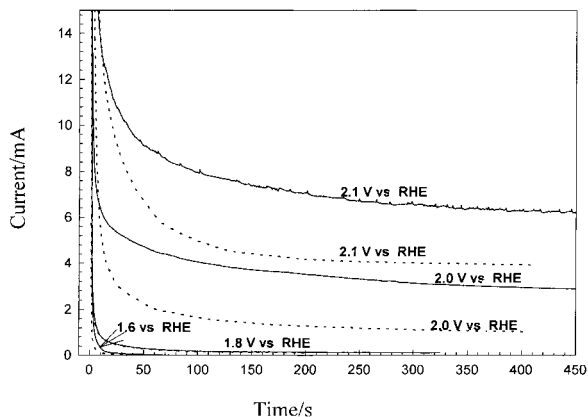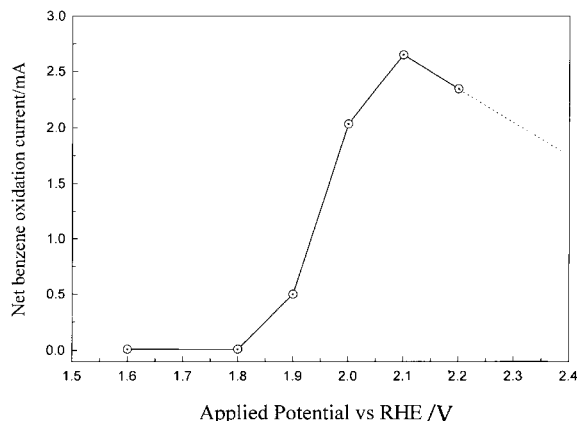

Fig. 4. Chronoamperograms for benzene-containing and background electrolytes at a GC electrode at several applied potentials. (Rotating rate 3500 rpm). Key: benzene oxidation (solid lines); background (dotted lines).
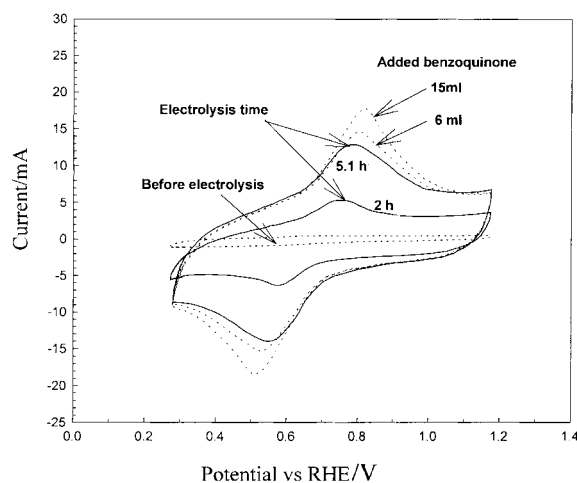

Fig. 6. Effects of electrolysis time at 2.1 V on a cyclic voltammogram at a GC electrode in benzene-containing electrolyte and after adding 0.22 M benzoquinone solution to the electrolyte solution after electrolysis at 2.1 V for 5.1 h. (Scan rate 100 mV s^{-1}).

mmogram recorded in the benzene-containing electrolyte before the electrolysis is indicated by the dotted lines in Figure 6 and showed no peaks at about 0.7 V. It should be noted that the current range for this case is very small, and that the potential range is 0.3 to 1.2 V, i.e. a range were there is no oxygen evolution taking place. However, after electrolysis at a potential of 2.1 V (sufficient for benzene oxidation on the basis of Figure 5), large cathodic and anodic currents were observed at the GC electrode. This suggests that the currents around 0.7 V are due to the oxidation and reduction of the product generated during the electrolysis, that is, the benzoquinone and not due to the direct oxidation of benzene at the electrode. The voltammogram obtained after storing the solution for one day following the electrolysis was the same as Figure 6. After the electrolysis, 6 ml and 15 ml of 0.02 M 1,4-benzoquinone (Aldrich) were added into 200 ml of solution and new cyclic voltammograms were recorded. These results also are shown in Figure 6 as dotted lines. The benzoquinone and hydroquinone peak currents increase linearly with the amount of added benzoquinone and the peak potentials shift a little to negative or positive directions, respectively. The expected concentration of benzoquinone in the solution after 5.1 hours of electrolysis at 2.1 V was estimated to be 1.31×10^{-3} M based on the net current for benzene oxidation. By using the linear relationship between the amounts of benzoquinone added into the solution and the peak currents for benzoquinone reduction, the concentration of benzoquinone in the solution generated by the electrolysis after 5.1 h was calculated to be about 1.21×10^{-3} M, about 90% of the expected concentration, and within

reasonable experimental error. This suggests that the main product of benzene oxidation is benzoquinone. The effect of scan rate in this electrolysis-product containing electrolyte was also examined. The oxidation and reduction peaks increased with an increase in scan rate similar to Figure 3, and they were found to be linear with the square root of scan rate.

The products formed during electrolysis were further analyzed by u.v. spectroscopy and by gas chromatography/mass spectroscopy. First, u.v. absorbance by the electrolyte before and after electrolysis clearly showed a diminishing absorbance at 209 nm due to benzene (Figure 7). A broad absorbance peak at about 245 nm became larger and broader following electrolysis but distinguishing benzene derivatives was not possible. In Figure 8, the total ionic chromatography (TIC) spectra before and after electrolysis of benzene-containing electrolyte are shown. In the case of before electrolysis, only one peak due to benzene is recorded. But after the electrolysis, peaks of p-benzoquinone and hydroquinone were dominant. Hydroquinone may be an intermediate oxidation product [3], or could be generated by the reduction of the p-benzoquinone at the cathode. It is known that p-benzoquinone is easily reduced to hydroquinone at a cathode in an undivided cell, like that employed in this work [18]. Also, a phenol peak is found, which is much smaller than those of p-benzoquinone and hydroquinone. The phenol peak is likely to be due to the benzene oxidation at the GC electrode [3, 4, 15], or from the reduction of the generated hydroquinone at the cathode [7, 19]. The small peak at the retention time of 11.5 min is that of 1-ethynyl-4-methylbenzene. All results in Figures 4 to 7 provide a
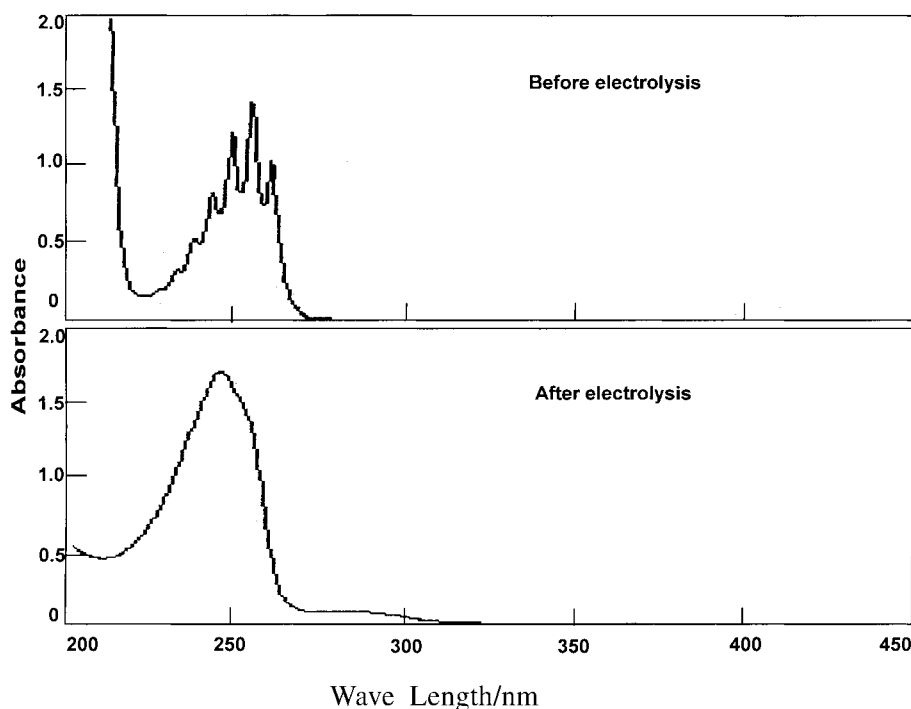

Fig. 7. Spectrophotometric spectra before and after electrolysis of benzene-containing electrolyte at a GC electrode.
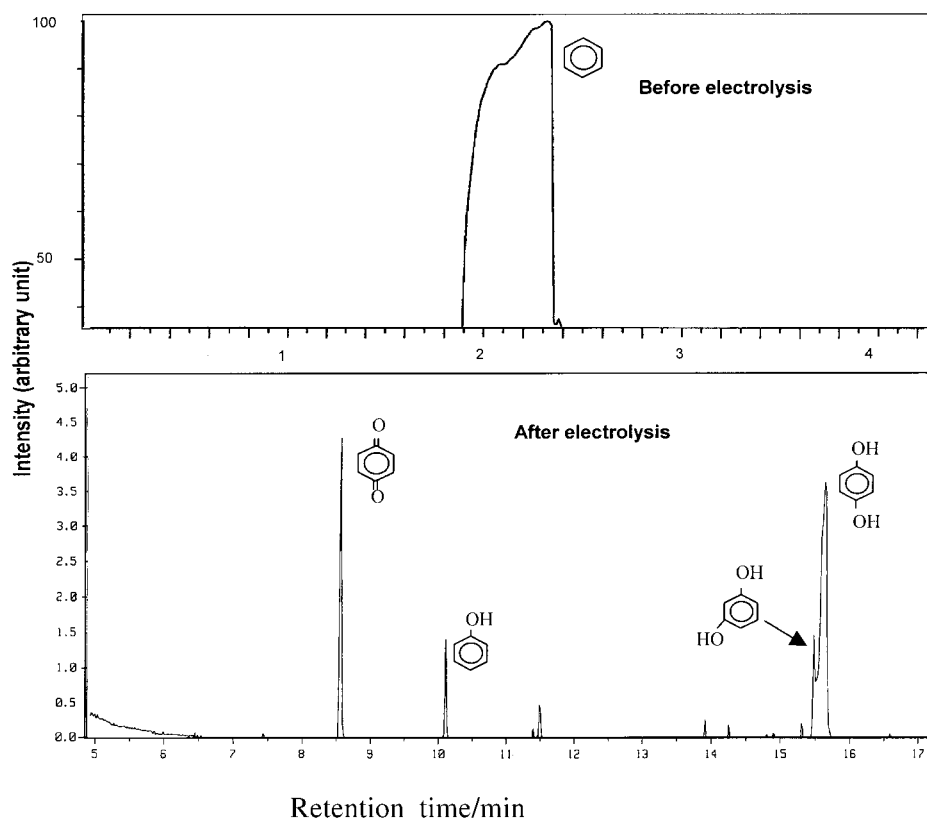
Fig. 8. TIC before and after electrolysis of benzene-containing electrolyte at a GC electrode.

convincing argument that indeed the GC electrode can be used for generating 'quinone-like' compounds from benzene solution. However, the results also suggest that the benzene oxidation products are subjected to reduction at the counter electrode. Consequently, a divided cell may be preferable for technical applications.

Figure 9 shows the cyclic voltammograms of benzene-containing and background electrolyte at GC and Pt electrodes. The voltammograms for the Pt electrode are

the same as those obtained by other researchers [20, 21]. In the voltammograms for the benzene-containing electrolyte at a Pt electrode, the peaks for the formation and oxidation of adsorbed hydrogen present in the background electrolyte disappear, and the benzene oxidation current occurs in the region of oxide layer formation above 1.0 V. The current for benzene-containing electrolyte at a GC electrode is about 10 times higher than that at a Pt electrode. The GC electrode is
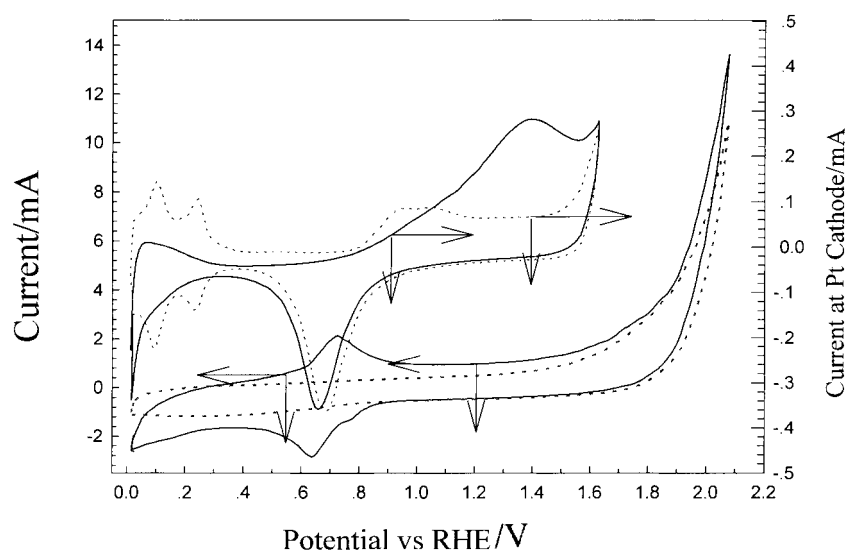

Fig. 9. Cyclic voltammograms for benzene-containing and background electrolytes at GC and Pt electrodes (Scan rate 100 mV s^{-1}). Key: benzene oxidation (solid line); background (dotted line).
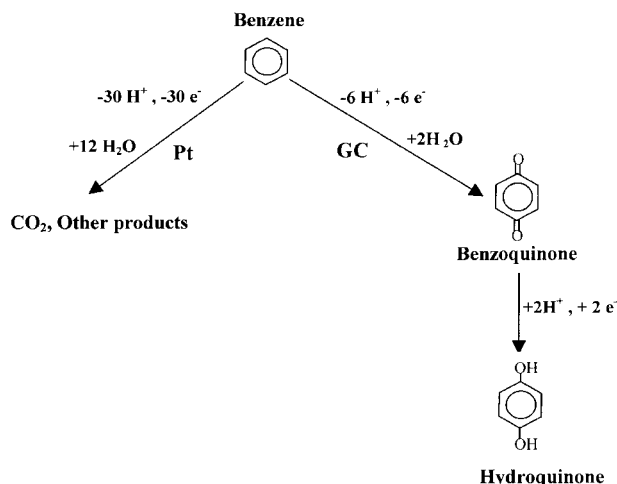
Fig. 10. Oxidation of benzene at Pt and GC electrodes.

observed to have 400 mV larger overpotential for oxygen evolution as compared to the Pt electrode. No peaks corresponding to reactions of benzoquinone and hydroquinone were seen for benzene-containing electrolytes at a Pt electrode. This suggests that a different mechanism of benzene oxidation occurs at a Pt electrode as compared to that of a GC electrode. It is known that the complete oxidation of benzene to carbon dioxide can occur readily at a Pt electrode [8, 22]. The two different reaction paths at GC and Pt electrodes are summarized in Figure 10. From all these results, a GC electrode may be suitable for production of benzoquinone and similar compounds from the benzene-containing solution.

4. Conclusions

Benzene is oxidized to benzoquinone by active oxygen adsorbed on a glassy carbon electrode in the oxygen evolution region. The glassy carbon electrode is suitable for generating benzoquinone and quinone-like compounds from benzene solution. In long-term operation the applied potential for benzene oxidation should be less than 2.1 V vs RHE to prevent electrode damage due to corrosion processes. The benzene oxidation mechanism and its products at glassy carbon appear to be different from those at platinum.

References

1. K.T. Chuang, S. Cheng and S. Tong, *Ind. Eng. Chem. Res.* **31** (1992) 11.
2. A.J. Bard, W.M. Flarsheim and K.P. Johnston, *J. Electrochem. Soc.* **135** (1988) 8.
3. J.C. Farmer, F.T. Wang, R.A. Hawley-Fedder, P.R. Lewis, L.J. Summers and L. Foiles, *J. Electrochem. Soc.* **139** (1992) 654.
4. I. Yamanaka, T. Akimoto and K. Otsuka, *Electrochim. Acta* **39** (1994) 2545.
5. K. Otsuka, M. Kunieda and H. Yamgata, *J. Electrochem. Soc.* **139** (1992) 2381.
6. J.S. Clarker, R.E. Ehigamusoe and A.T. Kuhn, *J. Electroanal. Chem.* **70** (1976) 333.
7. M. Gattrell and D.W. Kirk, *Canadian J. Chem. Eng.* **68** (1990) 997.
8. A.J. Bard, W.M. Flarsheim and K.P. Jonston, *J. Electrochem. Soc.* **135** (1988) 1939.
9. S. Kihara, Z. Yoshida and H. Aoyagi, *Bunseki Kagaku* **40** (1991) 309.
10. K.W. Kim, E.H. Lee, J.H. Yoo, *J. Appl. Electrochem.* submitted.
11. H. Holden Throp, *J. Chem. Educ.* **69** (1992) 250.
12. A. Proctor and P.M.A. Sherwood, *Carbon* **21** (1983) 53.
13. A.L. Belilby, T.A. Sasaki and H.M. Stern, *Anal. Chem.* **67** (1995) 976.
14. Allen J. Bard, 'Encyclopedia of Electrochemistry of Elements', Vol. 7 (Marcel Dekker, New York, 1976).
15. I. Yamanaka and K. Otsuka, *J. Electrochem. Soc.* **138** (1991) 1033.
16. G.E. Cabaniss, A.A. Diamantis, W.R. Murphy, Jr., W. Linton, and T.J. Meyer, *J. Am. Chem. Soc.* **107** (1985) 1845.
17. S. Ferro, F. Lavezzo, G. Lodi and A. DeBattisti, Extended Abstracts of the Electrochemical Society 193rd meeting, San Diego, Vol. **98-1** (1998) 874.
18. V. Smith, De Sugre and A.P. Watkinson, *Can. J. Chem. Eng.* **59** (1981) 52.
19. M. Gattrell and D. W. Kirk, *J. Electrochem. Soc.* **140** (1993) 1534.
20. M. Watanabe and S. Motoo, *J. Electroanal. Chem.* **60** (1975) 267.
21. M. Kuppuswamy, MS thesis, Case Western Reserve University, Cleveland, OH, USA (1998).
22. J. O'M Bockris, H. Wroblow, E. Gileadi and B. J. Piersma, *Trans. Faraday Soc.* **61** (1965) 2531.