Journal of Applied Electrochemistry **34**: 249–254, 2004.

Electrochemical oxidation of aniline at boron-doped diamond electrodes

M. MITADERA[1], N. SPATARU[1,2] and A. FUJISHIMA[3,*]
[1]*Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[2]*On leave from the Institute of Physical Chemistry of the Romanian Academy, 77208 Bucharest, Romania*
[3]*KAST, KSP Bldg., West 614, 3-2-1 Sakado, Takatsu-ku, Kawasaki-shi, Kanagawa, 213-0012, Japan*
*(*author for correspondence, e-mail: fujishima@kast.or.jp)*

Received 11 February 2003; accepted in revised form 14 October 2003

Key words: aniline, boron-doped diamond electrodes, electrochemical oxidation

Abstract

The electrochemical oxidation of aniline at boron-doped diamond (BDD) electrodes was investigated by cyclic voltammetry, steady-state polarization measurements and bulk electrolysis under potentiostatic control. It was found that acidic media is suitable for efficient electrochemical oxidation of aniline, because at low pH, the potential required for avoiding electrode fouling is lower than in neutral and alkaline media. The results of the longtime polarization measurements suggested that more anodic potentials ensure slightly higher efficiency for the conversion of aniline to CO_2, while the direct oxidation process does not play a prominent part in the overall electrochemical incineration of aniline. The current efficiencies (~44%) and the efficiency of aniline conversion to CO_2 (~80%) favourably compare with those reported for other electrochemical methods for aniline destruction. The results demonstrate the possibility of using BDD as an electrode material for electrochemical wastewater treatment, mainly when very high anodic potentials are required.

1. Introduction

Aniline is widely used in the chemical industry, mainly as raw material for obtaining isocyanate, an intermediate for the production of urethanes. Other principal applications include the production of accelerators and antioxidants for the rubber industry, the manufacture of intermediates for herbicides and other pesticides, and the manufacture of dyes and pigments. The amount of aniline produced in the United State is over 600 million kilograms per year, and the demand for this compound is expected to increase three to four percent per year [1]. The primary toxic effects resulting from exposure to aniline is the formation of methemoglobin and accompanying anoxia, erythrocyte damage and spleen effects [2].

The largest sources of aniline release are from its primary uses as a chemical intermediate in the production of polymers. Thus, it was estimated that in 1998, more than 0.6 million kilograms of aniline were released to the environment, mainly by underground injection or as surface water discharges [3]. For these reasons, there have been numerous studies devoted to the development of effective procedures for aniline-containing wastewater treatment, and several methods have been proposed, including photocatalytic degradation [4, 5], catalytic wet air oxidation [6], biodegradation [7,8], ultrasonic degradation [9], decomposition in supercritical water [10] and electrochemical techniques [11–16]. Although interest in the electrochemical approach is increasing, it should be noted that most of the electrochemical techniques for aniline degradation thus far reported rely either on electro-Fenton process (requiring that pure O_2 is supplied to the cathode, in order to produce hydrogen peroxide) [11–13], or upon mediated electrochemical oxidation [14, 15].

It is widely accepted that electrochemical oxidation is a promising technique for wastewater treatment and several model aromatic compounds have been used in order to assess the performances of different anode materials, including noble metals, porous carbon felt, and metallic oxide electrocatalysts [17–21]. Nevertheless, the low current efficiency and the rather poor stability of the anodes are still issues that remain to be addressed [22]. Conductive diamond represents an electrode material that has attracted great interest due to its outstanding electrochemical features: wide potential window in aqueous solutions, low background current and inertness to adsorption [23–26]. These unique properties, together with the extreme robustness and high resistance to corrosion, recommend polycrystalline diamond as an excellent electrode material for the anodic oxidation of organic wastes. In this respect, Comninellis and coworkers have reported several applications of diamond electrodes for wastewater treatment [22, 27–29].

This work was aimed at studying the electrochemical oxidation of aniline at boron-doped diamond (BDD) electrodes in order to evaluate the potential application of this electrode material for the electrochemical treatment of aniline-containing wastewater.

2. Experimental details

The boron-doped polycrystalline diamond coatings were deposited on Si(111) wafers by means of microwave plasma-assisted chemical vapour deposition, in accordance with a previously described procedure [26]. Electrochemical measurements were performed in a conventional three-electrode cell, at room temperature. BDD electrodes of 1 cm^2 area were used as working electrodes in the cyclic voltammetric measurements, while for the steady-state measurements and for the longtime polarization experiments the area of the working electrodes was 1.76 cm^2 and 3.14 cm^2, respectively. In all cases a platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) as reference.

The cyclic voltammograms were recorded with a Hokuto Denko HA-502 potentiostat, a Hokuto Denko HA 151 function generator, and a Riken Denshi X–Y recorder. A Hokuto Denko HZ-3000 potentiostat/galvanostat was used for the polarization measurements and for the potentiostatic electrolysis. Steady-state polarization measurements were carried out in stirred solutions, by applying increasingly positive potentials in 50 mV steps and then waiting for 3 min for the current to stabilize. Longtime polarization measurements were performed under potentiostatic control, with a volume of electrolyte solution of 70 cm^3. A 0.1 M Na_2SO_4 solution was used as supporting electrolyte in the polarization measurements, and the pH was adjusted by adding appropriate amounts of H_2SO_4 or NaOH standard solutions. Alternatively, for the cyclic voltammetric study, Britton–Robinson buffer solutions (containing 0.1 M Na_2SO_4), were used. UV–visible spectra were recorded using a Shimadzu UV-2400 PC spectrophotometer. Chemical oxygen demand (COD) was determined by the dichromate method. Thus, a volume of 2 cm^3 of sample was mixed with the required amount of reagent (Central Kagaku Corp., cat. no. 21259-25), the mixture was heated for two hours at 150 °C, and then the absorbance was checked (at a wavelength of 600 nm), with the same spectrophotometer.

Aniline (Special Grade from Wako) was used as received. All the other substances were analytical-reagent grade, and all solutions were prepared using Milli-Q water (Millipore).

3. Results and discussion

3.1. *Cyclic voltammetry*

The effect of pH on the aniline oxidation reaction at the BDD electrodes was investigated within the pH range 1.8–12.0. The cyclic voltammetric experiments were performed at a sweep rate of 100 mV s^{-1}, in a Britton–Robinson buffer solution (1 mM aniline), within the potential range 0.0–2.0 V. The literature dealing with aniline anodic oxidation is scarce, but attention has been given to the electrochemical formation of polyaniline films at potential values lower than ~1.4 V vs SCE [30–34]. Thus, to better understand the voltammetric behaviour of aniline at the BDD electrodes, we have compared our results with these.

Figure 1(a) shows voltammetric curves recorded for three consecutive runs, at pH 2.2. It can be seen that, during the first forward run, aniline oxidation results in the occurrence of two wave-shaped peaks (labelled I and II), with the half-peak potentials located at 1.05 V and 1.45 V, respectively. In addition, another small, ill-defined peak (labelled III) was observed within the potential range positive of peak II. It is widely accepted that, the first stage of the anodic oxidation of aniline (peak I in Figure 1(a)) involves the formation of nitrene cations of aniline, which by rapid follow-up reactions, give rise to dimeric products (e.g., *p*-aminodiphenylamine, benzidine) and polymeric films with emeraldine-like structure [30, 31, 35]. The same reaction path is suggested by the occurrence (at potential values lower than ~0.5 V) of a broad cathodic peak on the first reverse scan, followed by an anodic one during the second anodic sweep (Figure 1(a)). This is because it was shown that, in acidic media, the presence of this redox couple is undoubtedly due to the benzidine species [30]. It was also reported that, by applying higher anodic potential, emeraldine can be further oxidized to give a partly protonated nigrinaline polymer, followed by the formation of the full oxidized, insulating, pernigraline [32, 34]. Although under our experimental conditions (low aniline concentration and rather high sweep rate) long polymeric chains are probably not formed during the first anodic scan, it seems reasonable to assume that the occurrence of peaks II and III could be ascribed to a similar amine–imide gradual conversion.

As illustrated in Figure 1(a), further potential cycles result in a gradual decrease of the voltammetric response, indicating the fact that the electrode is blocked by reaction products. It is also interesting to note that, at low pH values, aniline oxidation seems to be affected in the early stage by the low conductivity of the reaction products adsorbed layer, even during the first anodic scan. This is not surprising, because it was previously showed that, at potential values above ~0.9 V vs SCE, polyaniline films are rather insulating [33, 34]. Nevertheless, we observed that these films can be completely removed from the BDD surface by applying high anodic potential (3.0 V) for a few minutes. After this anodic

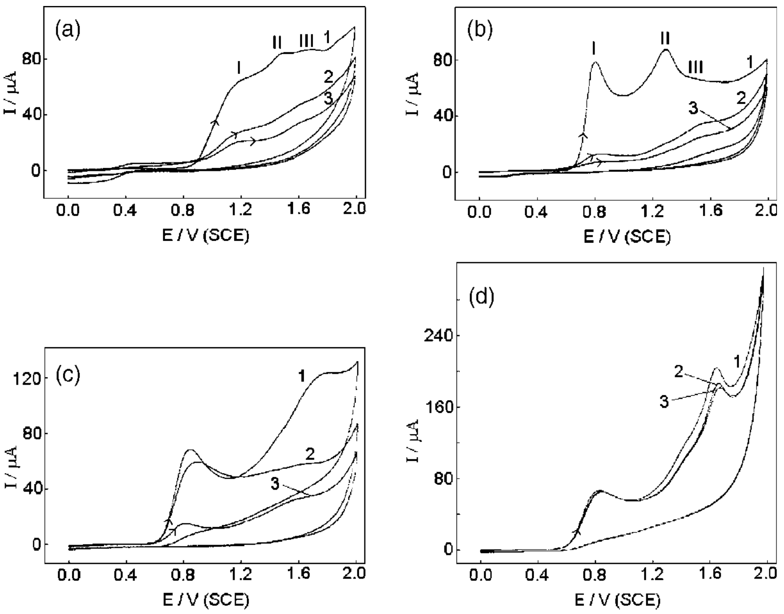

Fig. 1. Cyclic voltammograms in Britton–Robinson buffer containing 1 mM aniline: initial potential, 0.0 V (SCE); sweep rate 100 mV s^{-1}. (a) pH 2.2, (b) pH 5.2, (c) pH 8.7 and (d) pH 12.0. (Numbers indicate first, second and third sweep).

treatment, the cyclic voltammetric response is the same as in the first run.

The study of the effect of the pH on the voltammetric behaviour of aniline at the diamond electrodes showed that increasing pH (up to ~5.0) results in a gradual shift of the oxidation peaks towards lower potential values, as also reported for aniline oxidation at platinum electrodes [31]. Thus, as Figure 1(b) shows, during the first run at pH 5.2, the half-peak potentials of peaks I and II are located at 0.74 V and 1.20 V, respectively, and both peaks are well-shaped and well-separated. It is obvious that, aniline oxidation within the range of peak I is no more affected to a large extent by the low conductivity of the polymeric products, because the peak potential is located bellow 0.9 V. Furthermore, the shape of the voltammetric curve recorded during the first run indicates that the electroactive species are, at least in part, present into the solution and not confined at the electrode surface, as was the case at low pH (compare curves 1 from Figure 1(a) and (b)). This behaviour is in line with the observation that, in less acidic media, only a fraction of the aniline oxidation products are attached to the electrode, while another part is dissolved into the solution [35]. Nevertheless, it appears that further oxidation, at potential values positive of peak II, results again in blocking the electrode surface with reaction products, as indicated by curves 2 and 3 in Figure 1(b). It should be noted that, further increase of the pH up to ~7.5 did not result in significant changes of the voltammetric patterns.

A different behaviour was found for the aniline oxidation at the BDD electrodes in alkaline media. Thus, Figure 1(c) shows cyclic voltammograms recorded during consecutive scans at a pH value of 8.7. During the first scan, further oxidation of the aniline at anodic potentials higher than ~1.4 V is strongly enhanced, although this process seems to be still confined to the polymeric layer (as the shape of the corresponding voltammetric peak indicates), and does not result in the removal of the blocking films. Nevertheless, as shown in Figure 1(d), at higher pH (12.0) the final stage of the voltammetric oxidation of aniline seems to involve electroactive species that are present into the solution, rather than adsorbed at the BDD surface. This is an indication that, in strongly alkaline media and at high anodic potentials, insulating polyaniline films are less stable, probably due to the fact that they are more susceptible to be water-degraded [36]. The same conclusion is supported by the observation that no fouling of the BDD electrodes was observed during several consecutive voltammetric runs.

Aniline oxidation in aqueous electrolytes is actually a very complex process, involving several oxidation stages and deprotonation reactions, and the mechanism of the polymer formation, as well as their nature, depends to a large extent on the experimental conditions (aniline concentration, pH, polarization potential, polarization time) [32–35]. However, in the context of this work, the mechanism of polyaniline film formation has only a subsidiary connotation.

3.2. *Polarization studies*

The results of the cyclic voltammetric experiments indicated that, excepting strong alkaline media, the electrochemical oxidation of aniline at potentials lower than 2.0 V results in fouling of the electrodes, probably due to the adsorption of polymeric oxidation products. Therefore, it is likely that effective aniline degradation can occur only at potentials high enough to allow further oxidation of these products, ensuring the reactivation of the BDD electrodes.

To establish the most suitable conditions for this reactivation, steady-state polarization measurements were performed at several pH values, both in the absence and presence (5 mM) of aniline, and the results are shown in Figure 2. It seems reasonable to assume that, at the same potential, a current density in the presence of aniline (solid circles in Figure 2) lower than that in its absence (open circles) indicates that the surface of the BDD electrode is blocked by adsorbed oxidation products. The results of the steady-state measurements indicated that the potential required for the reactivation of the electrode surface gradually shifts towards higher values with increasing pH (insets in Figure 2). Unlike the cyclic voltammetry results, the polarization experiments showed that in strong alkaline media (Figure 2(c)) the stability of the adsorbed blocking layers is higher than in acidic and neutral solutions (Figure 2(a) and (b), respectively). A possible interpretation of this behaviour is provided by the fact that the formation of polymeric films by anodic oxidation of aniline is a slow process. It is therefore likely that at the time scale of the steady-state measurements these films are formed more readily than under cyclic voltammetry conditions.

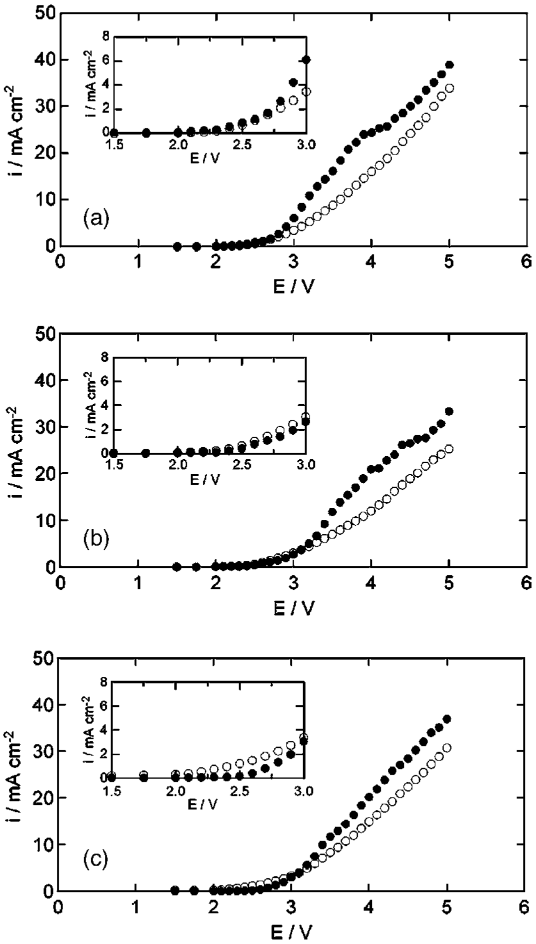

Fig. 2. Steady-state polarization curves in the absence of aniline (open circles) and at a concentration of 5 mM (solid circles) at several values of the pH: (a) pH 2.2, (b) pH 7.2 and (c) pH 11.9.

Nevertheless, as data in Figure 2 indicate, at potential values above those required for the reactivation of the electrodes, the oxidation of aniline takes place by direct electron transfer reactions on a BDD surface. Assuming that the increase in current evidenced by the polarization curves is due only to aniline oxidation, the current density for this process (Δi) can be estimated as the difference between the current density in the presence (i_t) and absence of aniline. Figure 3 shows the variation of Δi as a function of the applied potential, for several pH values. It can be observed that, the highest rate for direct aniline oxidation is achieved in acidic media, at a value of applied potential of ~3.8 V (curve 1 in Figure 3). Negative values of Δi in Figure 3 correspond to the potential ranges within which the surface of the BDD electrodes is blocked by the products of aniline oxidation. The variation of the ratio $\Delta i/i_t$ as a function of potential (Figure 4) suggests that the best efficiency (about 50%) for aniline direct oxidation is available in acidic media, for a value of applied potential of ~3.3 V. Due to the high anodic potential, aniline degradation by electrogenerated OH$^\bullet$ radicals is also likely to occur (together with oxidation by direct electron transfer at the BDD surface), and this process cannot be demonstrated by the polarization curves.

The results of the steady-state measurements suggested that at BDD electrodes acidic media is more suitable for efficient electrochemical treatment of aniline-containing wastewater. This is because at low pH the potential required for avoiding electrode fouling is lower than in neutral or alkaline media. Furthermore, acidic media ensure higher efficiency for aniline oxidation by direct electron transfer, which improves, to some extent, the efficiency of the overall oxidation process.

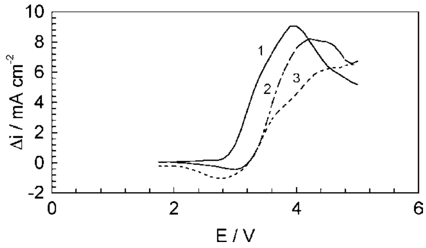

Fig. 3. Variation of the current density for direct oxidation of aniline as a function of the potential at several pH values: (1) pH 2.2, (2) pH 7.2 and (3) pH 11.9.

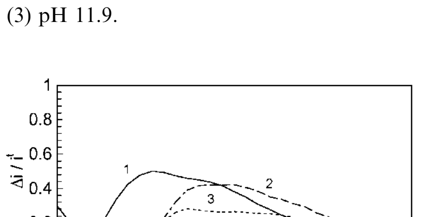

Fig. 4. Ratio of aniline direct oxidation current density on total current density as a function of potential at several pH values: (1) pH 2.2, (2) pH 7.2 and (3) pH 11.9.

3.3. *Longtime polarization measurements*

To assess the possibility of using BDD electrodes for electrochemical incineration of aniline, longtime potentiostatic polarization experiments were carried out in a 0.1 M Na_2SO_4 solution (pH 2.2) with a concentration of aniline of 1 mM. Electrolysis was performed at several values of applied potential and the chemical oxygen demand (COD) was periodically checked. It was observed that potentials higher than ~3.0 V resulted in a decrease in COD during electrolysis, and this behaviour is illustrated in Figure 5. At potentials above 3.0 V, the total decrease in COD was always higher than that predicted by aniline oxidation to NH_3 and CO_2. These findings indicate that, under the above experimental conditions, the complete degradation of aniline to CO_2 is better described by the following overall process [16]:

$$C_6H_5NH_3^+ + 15\,H_2O \rightarrow 6\,CO_2 + NO_3^- + 38\,H^+ + 36\,e^-$$

Figure 6 shows the variation with time of the efficiency of aniline conversion to CO_2, for two values of the applied potential. In both cases the conversion efficiency gradually increases, tending to reach a plateau after about 2 h. At more anodic potentials (curve 2 in Figure 6) conversion efficiencies are higher as higher currents flow at more positive potentials. Values of current efficiency (*CE*) for conversion of aniline to CO_2 were calculated using the following equation [16]:

$$CE = \frac{n/Q}{n_{th}/Q_{th}} \times 100$$

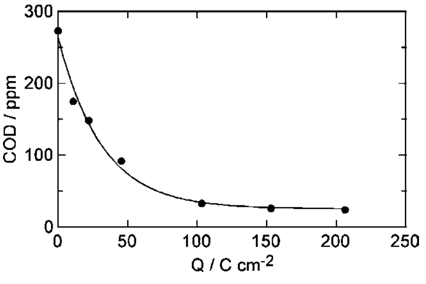

Fig. 5. Variation of COD as a function of total charge density during aniline potentiostatic oxidation. Aniline initial concentration: 1 mM; initial pH 2.2; applied potential 3.8 V.

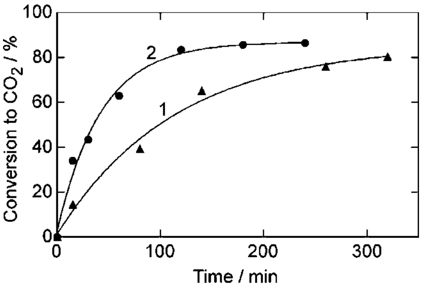

Fig. 6. Variation of efficiency of aniline conversion to CO_2 as a function of electrolysis time. Applied potential: (1) 3.3 V; (2) 3.8 V. (Other experimental conditions as in Figure 5).

where n and n_{th} are the number of moles produced or theoretically achieved respectively; and Q and Q_{th} is the actual or theoretical charge (in coulomb) passed or required, respectively.

To put the results of the longtime polarization measurements into a better perspective, Table 1 summarizes *CE* and the efficiency of aniline conversion to CO_2, for two values of applied potential. These data indicate that, for the same period of electrolysis, at more positive potentials the current efficiency decreases (probably due to stronger oxygen evolution), although the conversion efficiency is higher. It can be observed that, for the same amount of charge, slightly better conversion efficiency is available at a potential of 3.8 V. Table 1 shows that the current efficiency is almost the same for both potentials, in spite of the fact that a potential of 3.3 V ensures better efficiency for direct oxidation (as shown by curve 1 in Figure 4). Thus, although the direct oxidation of aniline at BDD electrodes can be demonstrated (unlike the case of other organic compounds [37]), it is reasonably to assume that this reaction does not play a prominent part in the overall process.

In the attempt to detect intermediate species, UV–visible spectra were recorded during electrolysis and the results are presented in Figure 7. To understand the nature of the intermediates better, we have compared our results with those previously reported for the destruction of aniline by mediated electrochemical oxidation [14]. It can be observed that, before applying the anodic potential, the spectra exhibit two bands at ~210 nm and ~250 nm, corresponding to n–π^* and π–π^* transitions of aniline (Figure 7, curve (a)). After

Table 1. Results obtained from aniline oxidation at BDD electrodes by electrolysis at constant potential. Aniline concentration: 1 mM, pH 2.2

Applied potential /V vs SCE	Electrolysis period /min	Total charge /C cm^{-2}	Conversion to CO_2 /%	*CE** /%
3.3	240	71.42	75	52
3.8	240	206.32	86	21
3.3	320	92.04	80	43
3.8	107	92.04	81	44

* Assuming a 36-electron process.

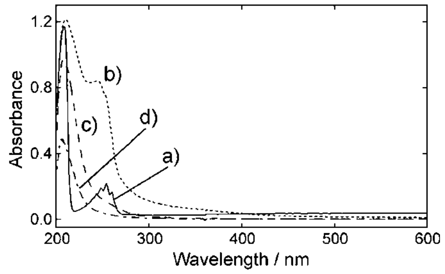

Fig. 7. UV spectra recorded during aniline potentiostatic electrolysis. Aniline initial concentration: 1 mM; initial pH 2.2; applied potential 3.8 V. Electrolysis period: (a) 0, (b) 30, (c) 120 and (d) 240 min.

30 min electrolysis (curve b) the band at about 250 nm is enhanced, probably due to the fact that, in the early stages, aniline oxidation results in the formation of *p*-benzoquinone, absorbing at about the same wavelengths. At the same time, the band at ~210 nm becomes broad, slightly overlapping that of *p*-benzoquinone. A possible explanation for this behaviour is provided by assuming the formation of maleic acid and maleic anhydride [14]. Data from Figure 7 suggests that, with further electrolysis (curves c and d), *p*-benzoquinone is almost completely destroyed, while some maleic acid is still present in the solution. It is noteworthy that, at electrode potentials higher than ~3.0 V, dimer species such as benzidine or dihydrazobenzene are not stable, as indicated by the absence of an adsorption band at about 420 nm. Although this interpretation of the UV–visible spectra should be only considered as tentative, our results agree quite well with previously reported data concerning aniline oxidation [14]. Nevertheless, further studies are under way in this laboratory to elucidate the effect of applied potential on the reaction path, and the nature of the intermediates.

4. Conclusions

Study of the anodic behavior of aniline at the BDD electrodes showed that acidic media is suitable for efficient electrochemical oxidation of this compound. This is because, at low pH, the potential required for avoiding electrode fouling is lower than in neutral and alkaline media. The results of longtime polarization measurements suggested that more anodic potentials ensure slightly higher efficiency for the conversion of aniline to CO_2, while a value of applied potential of ~3.3 V results in higher current efficiency. Unlike the case of other organic compounds, electrochemical incineration of aniline at BDD electrodes takes place not only by means of $OH^\bullet$ radicals, but also to some extent by direct electron transfer at the electrode surface. Nevertheless, this process does not play an important role in the overall electrochemical incineration of aniline. The current efficiencies and the efficiency of aniline conversion to CO_2 favourably compare with those reported for other electrochemical methods for aniline destruction. The results demonstrate the possibility of using BDD as an electrode material for electrochemical wastewater treatment, mainly when very high anodic potentials are required.

References

1. Report of the US Environmental Protection Agency, http://www.epa.gov/chemfact/anali-sd.txt.
2. N.I. Sax, ‘Dangerous Properties of Industrial Materials’ (Van Nostrand Reinhold Company, New York, 5th edn, 1979), p. 379.
3. Report of the National Safety Council, http://www.nsc.org/library/chemical/aniline.htm.
4. L. Sanchez, J. Peral and X. Domenech, *Electrochim Acta* **42** (1997) 1877.
5. E. Pramauro, A.B. Prevot, V. Augugliaro and L. Palmisano, *Analyst* **120** (1995) 237.
6. J. Barbier, L. Oliviero, B. Renard and D. Duprez, *Catal. Today* **75** (2002) 29.
7. R.W. Lowhorn, R.B. Bustamante and W.P. Bonner, *Fuel* **73** (1994) 1476.
8. H. Gheewala and A. Shabbir, *Water Sci. Technol.* **36** (1997) 53.
9. Y. Jiang, C. Petrier and T.D. Waite, *Ultrason. Sonochem.* **9** (2002) 163.
10. X.H. Qi, Y.Y. Zhuang, Y.C. Yuan and W.X. Gu, *J. Hazard. Mater.* **90** (2002) 51.
11. E. Brillas, E. Mur and J. Casado, *J. Electrochem. Soc.* **143** (1996) L49.
12. E. Brillas, R. Sauleda and J. Casado, *J. Electrochem. Soc.* **144** (1997) 2374.
13. E. Brillas, R. Sauleda and J. Casado, *J. Electrochem. Soc.* **146** (1999) 4539.
14. Y.H Chung and S.M. Park, *J. Appl. Electrochem.* **30** (2000) 685.
15. D.W. Kirk, H. Sharifian and F.R. Foulkes, *J. Appl. Electrochem.* **15** (1985) 285.
16. S.E. Treimer, J. Feng and D.C. Johnson, *J. Electrochem. Soc.* **148** (2001) E321.
17. J.A. Harrison and J.M. Maine, *Electrochim. Acta* **28** (1983) 1223.
18. D.C. Johnson, J. Feng and L.L. Houk, *Electrochim. Acta* **46** (2000) 323.
19. M. Panizza, C. Bocca and G. Cerisola, *Wat. Res.* **34** (2000) 2601.
20. G. Foti, D. Gandini and Ch. Comninellis, *Curr. Topics Electrochem.* **5** (1997) 71.
21. B. Bonfatti, S. Ferro, F. Levezzo, M. Malacarne, C. Lodi and A. DeBattisti, *J. Electrochem. Soc.* **146** (1999) 2175.
22. P. Montilla, P.A. Michaud, E. Morallon, J.L. Vazquez and Ch. Comninellis, *Electrochim. Acta* **47** (2002) 3509.
23. J.W. Strojek, M.C. Granger, T. Dallas, M.W. Holtz and G.M. Swain, *Anal. Chem.* **68** (1996) 2031.
24. T.N. Rao, I. Yagi, T. Miwa, D.A. Tryk and A. Fujishima, *Anal. Chem.* **71** (1999) 2506.
25. J.S. Xu, Q.Y. Chen and G.M. Swain, *Anal. Chem.* **70** (1998) 3146.
26. T. Yano, D.A. Tryk, K. Hashimoto and A. Fujishima, *J. Electrochem. Soc.* **145** (1998) 1870.
27. M. Panizza, P.A. Michaud, G. Cerisola and Ch. Comninellis, *Electrochem. Commun.* **3** (2001) 336.
28. M.A. Rodrigo, P.A. Michaud, I. Duo, M. Panizza, G. Cerisola and Ch. Comninellis, *J. Electrochem. Soc.* **148** (2001) D60.
29. B. Boye, P.A. Michaud, B. Marselli, M.M. Dieng, E. Brillas and Ch. Comninellis, *New Diamond Frontier Carbon Technol.* **12** (2002) 63.
30. J. Bacon and R.N. Adams, *J. Am. Chem. Soc.* **90** (1968) 6596.
31. R.N. Adams, ‘Electrochemistry at Solid Electrodes’ (Marcel Dekker, New York, 1969), p. 327.
32. W.S. Huang, B.D. Humphrey and A.G. MacDiarmid, *J. Chem. Soc. Faraday Trans. 1* **82** (1986) 2385.
33. D.E. Stilwell and S.M. Park, *J. Electrochem. Soc.* **135** (1988) 2497.
34. H.N. Dinh, P. Vanysek and V.J. Birss, *J. Electrochem. Soc.* **146** (1999) 3324.
35. F. Cases, F. Huerta, P. Garces, E. Morallon and J.L. Vazquez, *J. Electroanal. Chem.* **501** (2001) 186.
36. B. Wang, J. Tang and F. Wang, *Synth. Met.* **18** (1987) 323.
37. D. Gandini, P.A. Michaud, I. Duo, E. Mahe, W. Haenni, A. Perret and Ch. Comninellis, *New Diamond Frontier Carbon Technol.* **9** (1999) 303.