Electrosynthesis of 4,4′-dinitroazobenzene on PbO$_2$ electrodes

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Abstract

Parameters which affect the electrosynthesis of 4,4′-dinitroazobenzene from *p*-nitroaniline on platinum and PbO$_2$ electrodes were investigated and optimum conditions were determined. Maximum conversion efficiency for electrosynthesis was 95% with a pure β-PbO$_2$ electrode. It was found that the electrocatalytic activity of a PbO$_2$ electrode depends upon its α/β ratio and its degree of crystallinity. The effects of the added base and water on the conversion efficiency were also elucidated.

1. Introduction

PbO$_2$ is a preferred metal oxide electrode. The low electrical resistivity, good chemical stability and high oxygen overpotential are important characteristics of PbO$_2$ and it is known that these electrode properties are important for electrosynthesis [1, 2]. Lead dioxide has been used to make anodes suitable in preparative chemistry. Iodoform has been prepared using the reaction of acetone or ethanol at a lead dioxide anode in the presence of iodide ions [3]. Electrochemical generation of ozone was accomplished on a fluorine doped β-PbO$_2$ [4]. Doped bismuth lead dioxide anodes was used for anodic oxidation of phenol in aqueous solution [5]. Iodine has been anodized to periodic acid using lead dioxide electrodes with high current efficiencies [6, 7]. In all of these investigations lead dioxide behaves as an inert electrode in much the same way as Pt, rather than showing any specific electrode catalytic activity.

It is well known that PbO$_2$ exists in two different crystallographic forms (α and β) [8]. α-PbO$_2$ has a lower electron mobility and higher electron concentration compared to β-PbO$_2$. The effect of the electron mobility overcompensates that of the electron concentration so that the conductivity of α-PbO$_2$ is almost one order of magnitude lower than that of β-PbO$_2$ [9]. The electrical conductivity is important for it is also known that the amount of the β form and the degree of the crystallinty of PbO$_2$ films can be changed by adding controlled amounts of water to nonaqueous solvent acetonitrile and adjusting other electrochemical parameters during the electrodeposition [10]. In oxygen evolution, the β-form is known to be much more electrocatalytically active than the α-form [11].

Azo compounds are of tremendous importance as dyes and acid–base indicators in both industrial and laboratory use because they are classified as strong colour agents and their colours vary with the exact structure of the molecules [12]. In the chemical synthesis of azo compounds, an aniline molecule reacts with another one in acidic media to form diazonium salts and these salts usually cause formation of azo compounds. The aromatic ring has to contain a strong electron-releasing group, such as —OH, —NR$_2$, —NHR, NH$_2$ etc., at the *para* site to carry out this kind of synthesis. Based on this information, it can be concluded that synthesis of the azo compounds from anilines substituted with a powerful electron-withdrawing group is difficult via chemical methods [13]. It is the aim of this study to use lead dioxide surfaces as electrodes in the electrosynthesis of 4,4′-dinitroazobenzene from *p*-nitroaniline.

2. Experimental details

The procedure used to purify acetonitrile (Merck) has been described elsewhere [14, 15]. Tetrabutylammonium perchlorate (TBAP) was prepared by reacting concentrated perchloric acid solution (Analar) with a 40% aqueous solution of tetrabutylammonium hydroxide (Aldrich). It was recrystallized from ethanol several times and kept under a nitrogen atmosphere after vacuum drying for 24 h at 120 °C. Lead perchlorate (Pb(ClO$_4$)$_2$) was prepared by reacting concentrated perchloric acid with lead monoxide (Analar). All electrochemical experiments were carried out under a nitrogen (BOS) atmosphere. The electrochemical cell used

was of the three electrode type with separate compartments for the reference electrode (Ag, AgCl (sat)) and the counter electrode (platinum spiral). The acetonitrile + 0.1 M TBAP solution in the reference electrode compartment was saturated with AgCl. The working electrodes were a platinum disc (0.0132 cm^2) and a macro platinum electrode (3 cm^2).

Electrolyses for obtaining 4,4′-dinitroazobenzene from p-nitroaniline were carried out using a divided cell. The volume of the catholyte and anolyte were 15 ml. Nafion$^®$ 117 membrane was used as separator. Electrolyses periods changed depending on the type of the working material (45–300 min). 40 C was consumed for each electrolysis. Electrolyses were stopped when the oxidation current decreased to the value of the residual current.

A pure β-PbO$_2$ (100% β) surface was electrodeposited from a solution which had 6 M H$_2$O and 100 mM PbClO$_4$ solution in acetonitrile + 0.1 M TBAP with a current density of 50.0 mA cm^{-2}.

A pure α-PbO$_2$ (100%) film was prepared using 100 mM aqueous PbClO$_4$ solution containing saturated amount of PbO with a current density of 4 mA cm^{-2}.

PbO$_2$ films with had different α and β modifications and degrees of crystallinities were prepared according to the procedure described in [10]. The relative degree of crystallinity of the films was calculated using the half-width values of the XRD lines, as previously reported [16]. α and β modifications of PbO$_2$ were distinguished from each other by means of X-ray diffraction patterns and these patterns were used to estimate the proportions of the polymorphs in a mixture of the two [17].

The electrochemical instrumentation consisted of a PAR (model 173) potentiostat–galvanostat coupled to a PAR (model 175) universal programmer and a PAR (model 179) digital coulometer, and also PAR (model 273) potentiostat–galvanostat.

GC/MS instrumentation consisted of an HP 6890 gas chromatograph coupled to an HP 5972A quadrupole mass spectrometer (Hewlett-Packard). The gas chromatograph was equipped with a 30 m × 0.25 i.d. (0.25 μm film thickness) HP-5MS capillary column (Hewlett-Packard). Injections (0.2 μl) were made in the split mode with the split ratio set to 20:1. Helium was used as the carrier gas at a head pressure of 76 kPa. The injector temperature was 250 °C and the column temperature programme was initially 120 °C for 2 min, and then was increased from 120 °C to 280 °C at 10 °C min^{-1}. The GC/MS interface temperature was 280 °C.

The mass spectrometer was operated under electron impact ionization conditions with the following source parameters: electron energy, 70 eV; emission current, 300 μA; and source temperature, 180 °C.

3. Results and discussion

Electrosynthesis solution was prepared by adding 10 mM p-nitroaniline as starting material and 0.1 M TBAP as supporting electrolyte to non aqueous solvent
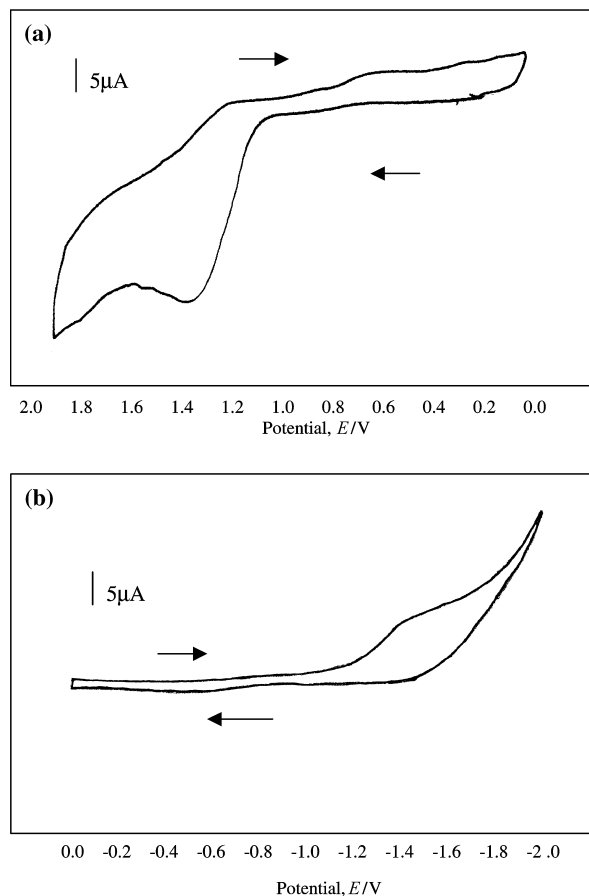

Fig. 1. Voltammogram of the electrolysis solution in anodic region (a) and cathodic region (b). Pt working electrode, scan rate 100 mV s^{-1}.

acetonitrile. 25 mM pyridine was also added since electrosynthesis of azo compounds are favoured in basic medium [18]. Cathodic and anodic voltammograms of this solution are shown in Figure 1. The oxidation peak of p-nitroaniline is observed at a potential of about +1.35 V vs Ag/AgCl in this solution and the reduction peak of nitro group appears at −1.40 V vs Ag/AgCl.

Electrolysis of p-nitroaniline was carried out at a constant potential of +1.40 V vs Ag/AgCl with pure β-PbO$_2$, pure α-PbO$_2$ and Pt electrodes in order to obtain 4,4′-dinitroazobenzene by electrochemical methods. Electrolysis was maintained until the charge passed during the process reached the value which was theoretically sufficient to convert all the p-nitroaniline to 4,4′-dinitrazobenzene. Electrolysed solutions were analysed by cyclic voltammetry, coulometry and the GC-MS technique. It was determined that platinum and α-PbO$_2$ electrodes did not cause the formation of any 4,4′-dinitroazobenzene. However, the pure β-PbO$_2$ electrode converted most of the p-nitroaniline to 4,4′-dinitroazobenzene. The conversion efficiency was 95%. One side product was obtained in electrolyzed solution and was identified as 4-nitro-4-aminoazobenzene. The cathodic and anodic voltammograms of the electrolysed solution are shown in Figure 2. In the anodic region, the oxidation peak of
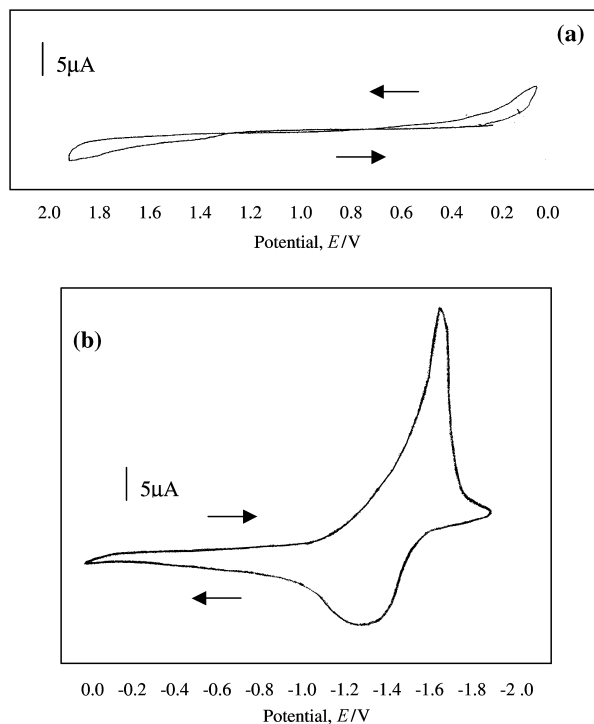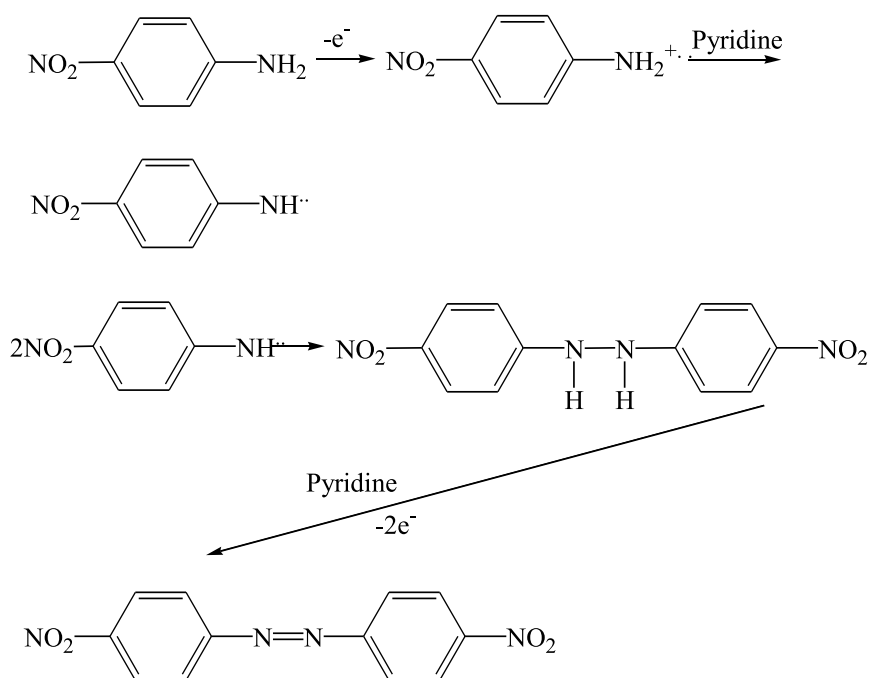
Fig. 2. Voltammogram of the electrolysed solution in anodic region (a) and cathodic region (b). Pt working electrode, scan rate 100 mV s^{-1}.

Table 1. Change in conversion efficiency with α, β amounts of PbO$_2$ Degree of crystallinity of PbO$_2$ films are close to each other.

Crystal structure of PbO$_2$		Conversion efficiency/%
α/%	β/%	
–	100	95
5	95	84
16	84	70
28	72	65
39	61	40
68	32	negligible
100	–	–

The conversion efficiency changed with the α/β ratio and the degree of crystallinity of PbO$_2$ films. As can be seen from Table 1, conversion efficiencies decreased with increasing amounts of the α form. PbO$_2$ electrodes which have more than 15% α modification caused the occurrence of a black layer on the electrode and a black precipitate in the solution. This black precipitate increased with increasing amounts of α form and could not be dissolved in any organic solvent. This material might be a tar or a polymeric product, as previously reported [13, 18]. These results indicate that the β form of PbO$_2$ has higher catalytic activity in this electrosynthesis process.

As mentioned above, the differences in the degree of crystallinity of PbO$_2$ films also caused variations in conversion efficiencies. Figure 3 shows the change in conversion efficiency with the degree of crystallinity of the β-PbO$_2$ films. The higher the degree of crystallinity the higher the yield of product.

To determine the effect of basicity on electrosynthesis, the pyridine concentration in the electrolysis solution

p-nitroaniline disappeared and in the cathodic region, the reduction peak of 4,4′-dinitroazobenzene was observed. Similar cathodic electrochemical behaviour for 4,4′-dinitroazobenzene was observed under the same conditions. The mechanism of the conversion is shown in Scheme 1.

Scheme 1.

Fig. 3. Change in conversion efficiency with the degree of crystallinity of β-PbO$_2$ film.

Table 2. Change in conversion efficiency with the amount of water added to electrolysis solution when pure β-PbO$_2$ electrode was used

Water concentration/mol l^{-1}	Conversion efficiency/%
–	95
10	67
20	34
30	17

described above was increased and electrolysis was carried out using a pure β-PbO$_2$ electrode. It was found that the conversion efficiency decreased with increasing amounts of pyridine due to the fact that increasing amounts of the β form were converted to α form during the electrocatalytic activity of the surface in alkaline solutions [19].

The electrooxidation was also carried out with a pure β-PbO$_2$ electrode by adding controlled amounts of water to the electrosynthesis solution. Upon addition of water, a brownish adsorbed layer was formed on the electrode surface. This layer was dissolved in acetonitrile and found to consist of 4,4′-dinitroazobenzene when analysed by the methods mentioned above. Adsorbed product was favored because of the solubility limitations as water was added. It was also observed that increasing amounts of water decreased the conversion efficiency. This may be due to the increase in the amount of the adsorbed layer on the electrode which blocks the active sites and lowers the catalytic activity. Another reason may be the concurrent decomposition of the added water at the electrolysis potential. These results are summarized in Table 2. Electrolysis could not be carried out in aqueous solutions containing more than 30 M water.

It can be concluded that the polymorphic composition and the degree of crystallinity of the electrodeposited PbO$_2$ surface and the basicity and the water content of the electrolysis solution have pronounced effects on the yield of the electrooxidative formation of 4,4′-dinitroazobenzene from *p*-nitroaniline in acetonitrile medium.

References

1. I.H. Yeo, Y.S. Lee and D.C. Johnson, *Electrochim. Acta* **37** (1992) 1811.
2. M. Couper, D. Pletcher and F. Walsh, *Chem. Rev.* **90** (1990) 837.
3. R. Ramaswamy, M.S. Venkatachalapathy and H.V.K. Udupa. *J. Electrochem. Soc.* **110** (1963) 294.
4. R. Amadelli, L. Armelao, A.B. Velichenko, N.V. Nikolenko, D.V. Girenko, S.V. Kovalyov and F.I. Danilov, *Electrochim. Acta* **45** (1999) 713.
5. N.B.Tahar and A. Savall, *J. Appl. Electrochem.* **29** (1999) 277.
6. T. Osuga and K. Sugino, *J. Electrochem. Soc.* **104** (1957) 448.
7. Y. Aiya, S. Fujii, K. Sugino and K. Shirai, *J. Electrochem. Soc.* **109** (1962) 419.
8. V.H. Dodson, *J. Electrochem. Soc.* **108** (1961) 406.
9. W. Mindt, *J. Electrochem. Soc.* **116** (1969) 1076.
10. S. Abaci, K. Pekmez, T. Hökelek and A. Yildiz, *J. Power Sources* **88** (2000) 232.
11. P. Ruetschi, J. Sklarchuk and R.T. Angstadt, *Electrochim. Acta* **8** (1963) 333.
12. R.T. Morrison and R.N. Boyd, 'Organic Chemistry', 5th edn (Allyn and Bacon, MA, 1987), p. 978.
13. F. Porta, F. Colonna, F. Arciprete, S. Banfi and F. Coppa, *J. Mol. Catal.* **113** (1996) 359.
14. M. Walter and L. Ramaley, *Anal. Chem.* **45** (1973) 165.
15. M. Sertel, A. Yíldíz and H. Baumgartel, *Electrochim. Acta* **31** (1986) 1625.
16. D. Kordes, *Chem. Ing. Tech.* **38** (1966) 638.
17. N. Munichandraiah, *J. App. Chem.* **22** (1992) 825.
18. S.Wavzonek and T.W. Mc Intyre, *J. Electrochem. Soc.* **114** (1967) 1025.
19. N.E. Bagshaw, R.L. Clarke and B. Halliwell, *J. App. Chem.* **16** (1966) 180.