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ORIGINAL PAPER

Azobenzene-modified oxygen-fed graphite/PTFE electrodes for hydrogen peroxide synthesis

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Abstract The performance of a catalyzed H_2O_2 electrogeneration process using a modified oxygen-fed graphite/PTFE electrode is reported. The organic redox catalyst chosen for incorporation into the graphitic mass was azobenzene. The yield of the hydrogen peroxide is related to the applied potential and to azobenzene concentration. Modification of the gas diffusion electrode with azobenzene improved hydrogen peroxide production, and the overpotential for oxygen reduction was shifted to less negative values compared to the performance of a non-catalyzed electrode, indicating that these modified electrodes have good electro-activity.

Keywords Hydrogen peroxide · Gas diffusion electrodes · Azobenzene · Electrochemistry

1 Introduction

Hydrogen peroxide is one of the most popular non-selective oxidizing reactants for the oxidation of organic pollutants to carbon dioxide. Hydrogen peroxide is manufactured today almost exclusively by the autooxidation of 2-ethyl-9,10-dihydroxyanthracene to 2-ethylanthraquinone and hydrogen peroxide using oxygen from the air. The anthraquinone derivative is then extracted and reduced back to the dihydroxy compound using hydrogen gas in the presence of a metal catalyst. The overall equation for the process is deceptively simple: $H_2 + O_2 \rightarrow H_2O_2$. However the economics of the process depend on effective recycling of the quinone and extraction solvents, and of the hydrogenation catalyst [1, 2]. Formerly inorganic processes were used, employing the electrolysis of an aqueous solution of sulfuric acid or acidic ammonium bisulfate (NH_4HSO_4), followed by hydrolysis of the peroxydisulfate $((SO_4)_2)^{2-}$ which is formed [1].

Some studies have reported the oxygen reduction reaction on electrodes modified with quinones [3–13] and azobenzene [14–19]. The electrochemical behavior of azobenzene and its derivatives in solution has been studied extensively because of the involvement of proton transport, adsorption/desorption, and cis-trans isomerization [20–24]. A number of studies have investigated gold electrodes modified by adsorption of azobenzene derivative compounds [15–19].

Zhang et al. [15] studied the electrochemical performance of self-assembled azobenzene derivative monolayers on gold. Cyclic voltammetry shows the relation between oxidation/reduction peaks and scan rate. At a low scan rate, voltammetric responses corresponding to an irreversible two-electron, two-proton reduction/oxidation of the *trans*-azobenzene redox center were obtained in the range +300 mV to –800 mV (SCE), which exhibited very large peak-to-peak splitting. At a high scan rate of 500 mV s^{-1}, a two step reversible one-electron, one proton reduction/oxidation corresponding to the *cis*-azobenzene was clearly observed between +300 mV and –200 mV (SCE).

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When the –N=N– moiety is reduced to –HN–NH–, the large π-electron conjugated system between the two benzene rings is broken. The reduced –HN–NH– can be considered an electron-donor group. Therefore, the chemical environment in the reduced monolayer should be very different from that of the oxidized case. A large variation in the electron density and dipole moment in the benzene rings and their substitute groups are expected [19].

Liu Z-F et al. [16–19] studied the electrochemical behavior of azobenzene self-assembled monolayers of different structures in aqueous solution. It was found that the redox reaction of azobenzene group in the monolayer on gold electrode was a $2e^-/2H^+$ process and the redox behavior was greatly affected by the monolayer structure.

Sljukic et al. [14] reported the electrochemical reduction of oxygen using glassy carbon or edge plane pyrolytic graphite electrodes modified with azobenzene, hydroazobenzene or fast black K salt. The voltammetry of azobenzene at an edge plane pyrolytic graphite electrode in a pH 2 phosphate buffer solution shows a reduction peak at –0.6 V (SCE), which corresponds to the reduction of azobenzene to hydroazobenzene. The corresponding oxidation peak is observed at +0.4 V (SCE). When the voltammetric window was extended to more negative potentials, the hydroazobenzene was irreversibly reduced to aniline at –1.2 V (SCE) [14, 25, 26]. Comparison of oxygen reduction at the unmodified glassy carbon electrode and a glassy carbon electrode modified with azobenzene reveals that the oxygen wave in the latter case shifts to less negative potentials from –0.53 V to –0.37 V (SCE), with a significant increase in the peak current, suggesting good electro-activity [14].

Taking a different approach, this paper reports the incorporation of different concentrations of azobenzene into the gas diffusion electrodes for the electrosynthesis of hydrogen peroxide in dilute acidic solutions. Furthermore, larger-area electrodes were produced and used for the optimization of H_2O_2 generation rate relative to potential and the catalyst concentration.

2 Experimental

2.1 Azobenzene behavior

Preliminary cyclic voltammetry experiments were performed to identify azobenzene redox reactions in a non-aqueous medium containing vacuum-distilled dimethylformamide (DMF) plus dried $NaClO_4$ 0.1 M (pH 7.0). A three-electrode arrangement was used in the electrochemical cell (one compartment, 100 ml) with glassy carbon (3 mm diameter) serving as the working electrode, a platinum foil used as the counter electrode, and Ag/AgCl (KCl sat.) as reference electrode. The glassy carbon disk electrode (Metrohm) was first polished with 0.1 µm Al_2O_3 powder until a mirror-like surface was obtained. Cyclic voltammograms were recorded in the non-aqueous medium with 60 mM azobenzene (AZO), at different scan rates (20, 50, 100, 200, 300, 400, 500 mV s^{-1}), after N_2 purging (30 min).

All experiments were controlled by a PGSTAT30 potentiostat/galvanostat connected to a BSTR-10A Current Booster (Autolab).

2.2 Electrode preparation

The modified gas diffusion electrode (MGDE) precursor mass was prepared from Degussa Printex 6L conductive carbon-black graphitic pigment. As hydrophobic binder, a 60% polytetrafluoroethylene dispersion (Dyneon TF 5035 PTFE) was used. The ratio of Printex to PTFE was 8/3.3, which is equivalent to 20% of PTFE. The mixture was homogenized in a 4:1 bi-distilled water:isopropanol solution. The selected amounts of azobenzene, from 0.5 to 10%, relative to the carbon pigment, were incorporated into the MGDE precursor mass, which was dried at 110 °C for 24 h. A 200 mesh AISI 304 stainless steel screen current collector was placed at the bottom of a 60 mm diameter pressing tool, which was then filled with 8 g of the precursor mass. Sintered 3 mm thick MGDE was obtained after 1.5 h at 310 °C, under a load of 18 MPa.

2.3 MGDE behavior

In a further series of experiments, GDE prepared with different concentrations of AZO (0.5, 1, 3, 5 and 10%) was used as cathode (MGDE). For voltammetric and electrolysis experiments, an electrochemical cell (one compartment, 250 ml) was used [13]. The MGDE was placed at the bottom of the cell with an exposed area of 19 cm^2, and the electrode was oxygen-back-fed. The reference was Ag/AgCl (KCl sat.), and a platinum foil was the counter electrode ($A = 24\ cm^2$). This electrochemical cell was thermostatted at a constant temperature of 20 °C. The supporting electrolyte was 0.1 M H_2SO_4 plus 0.1 M K_2SO_4, pH 1. Experiments were performed under mechanical agitation.

The linear voltammetry was recorded from –0.1 V to –1.0 V vs. Ag/AgCl at 20 mV s^{-1}. The supporting electrolyte was previously saturated with nitrogen. Afterwards, i/E responses were also recorded in the presence of oxygen.

Subsequently, controlled potential electrolysis was used for the optimization of H_2O_2 electrogeneration rate relative to the applied potential in the range $-0.5 \leq E \leq -0.9$ V vs. Ag/AgCl. During electrolysis an oxygen pressure of 0.16 bar was maintained on the back side of the electrode. The electrolyte was sampled at intervals of 5 min for the first half hour, and every 10 min after that. Electrolysis experiments were performed in duplicate.

Hydrogen peroxide concentration was determined by a UV-Vis spectrophotometer (Lambda 40, Perkin Elmer Instruments), recording the spectra over 200–500 nm. A solution of 2.4 mM $(NH_4)_6Mo_7O_{24}$ $4H_2O$ in 0.5 M H_2SO_4 was added to the samples, resulting in a yellow color [27]. The absorbance was determined at 350 nm. Calibration plots based on Beer-Lambert's law were established relating absorbance to concentration.

3 Results and discussion

3.1 Azobenzene behavior

The experiments in a non-aqueous solvent were performed to identify azobenzene redox reactions. The azobenzene is used as an electrocatalyst, and the AZO-cycle is responsible for the O_2 reduction to hydrogen peroxide. Figure 1 shows a cyclic voltammogram recorded on glassy carbon for the non-aqueous solution containing 60 mM of AZO in the potential range 0.0 V to –1.0 V vs. Ag/AgCl, at different scan rates. A pair of peaks denoted by (a) and (b), almost 430 mV apart, is observed. The reduction peak is found at –0.79 V (Ag/AgCl), which corresponds to the reduction of azobenzene to hydroazobenzene, and the associated oxidation peak is at –0.35 V (Ag/AgCl). As mentioned, one cathodic peak and one anodic peak correspond to a trans-azobenzene/azobenzene redox couple, assuming a two-proton and two-electron reaction mechanism [15–17] (Scheme 1). This behavior was observed regardless of scan rate; this differs from Zhang et al. [15], who report that voltammetric behavior varies with the scan rate.

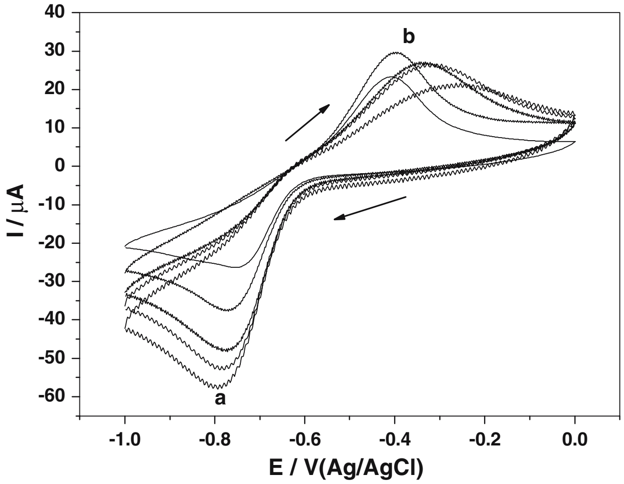


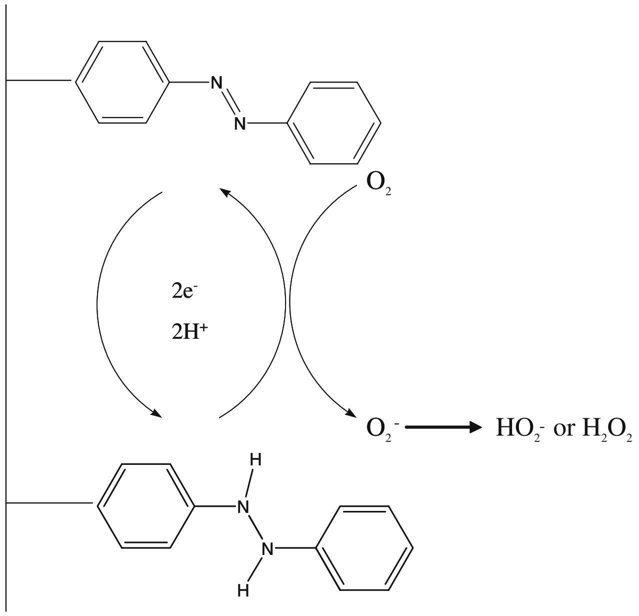
Fig. 1 Cyclic voltammogram on glassy carbon in non-aqueous solution (DMF/$NaClO_4$ 0.1 M, pH 7) plus 60 mM azobenzene, at different scan rates: 50, 100, 200, 300 and 500 mV s^{-1}, after N_2 purging (30 min)

The oxygen reduction reaction was studied using cyclic voltammetry on glassy carbon in a DMF/$NaClO_4$ solution and a DMF/$NaClO_4$ plus 60 mM AZO solution, as shown in Fig. 2. The curve for the DMF/$NaClO_4$ plus 60 mM AZO oxygen-saturated solution displays the beginning of the oxygen reduction reaction displaced to a less negative potential, and a significant peak current increase, suggesting good electro-activity in the presence of azobenzene.

3.2 MGDE behavior

3.2.1 *Voltammetric experiments*

MGDE electrodes prepared with different concentrations of AZO were used as cathodes in aqueous medium for the synthesis of hydrogen peroxide (0.1 M H_2SO_4 plus 0.1 M K_2SO_4, pH 1). Currents of AZO reduction



Scheme 1 Overall reaction pathway for the oxygen reduction reaction mediated by azobenzene redox catalyst

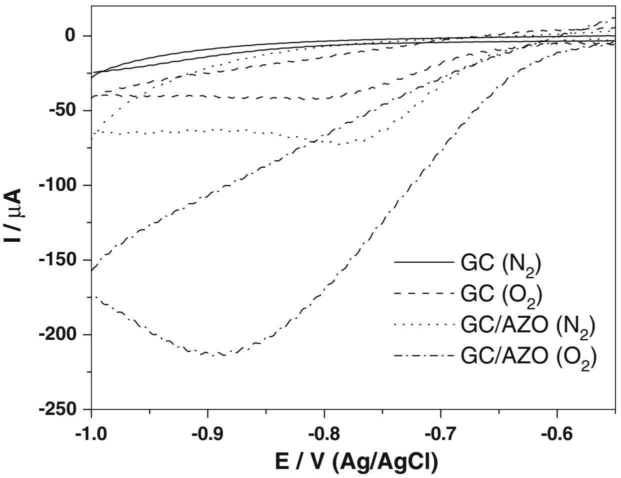


Fig. 2 Cyclic voltammogram on glassy carbon in a: DMF/$NaClO_4$ and DMF/$NaClO_4$ plus 60 mM AZO solution. Solution saturated with nitrogen or oxygen (15 min). Scan rate of 100 mV s^{-1}

recorded in these experiments were proportional to AZO concentration. Figure 3A shows a linear potential scan for the MGDE in 250 ml of supporting electrolyte. Once the solution was thoroughly nitrogen-purged, currents were related to the reduction of AZO.

Figure 3B shows the voltammetric response when the MGDE was fed with oxygen for different AZO concentrations. Current values recorded in these experiments are probably a result of two simultaneous processes: direct oxygen reduction on the graphite surface and AZO reduction. When the catalyst concentration was increased an increasing current response was observed as a consequence of a reduction in the overpotential demanded for the oxygen reduction reaction.

3.2.2 Electrolysis at controlled potential

All six electrodes with 0–10% of AZO were tested for the synthesis of hydrogen peroxide. They were oxygen-fed under 0.16 bar pressure and bulk electrolysis was carried out with potentials from –0.5 V to –0.9 V vs. Ag/AgCl. Hydrogen peroxide concentration was monitored for the 60 min of the experiments. Figure 4 shows a representative plot of hydrogen peroxide concentration as a function of electrolysis time for the potential values shown using a MGDE (10% AZO). All electrodes displayed similar rising concentration profiles. The concentration curves in Fig. 4 show that slopes increase from –0.5 V to –0.7 V vs. Ag/AgCl, and subsequently decrease. Higher potential values stimulate water production in a four-electron reaction.

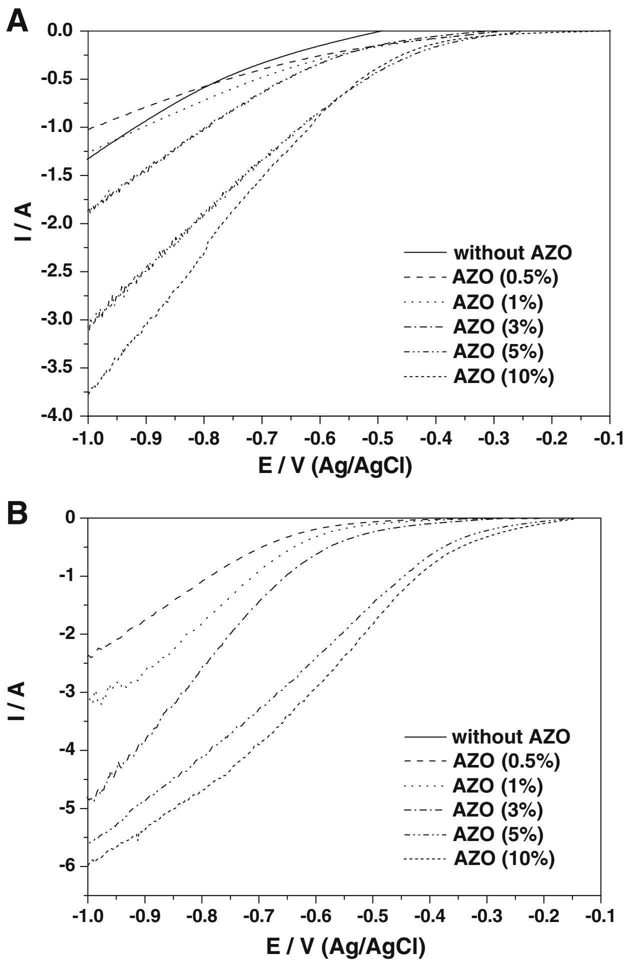


Fig. 3 Currents recorded for a linear potential scan on the MGDE surfaces with AZO concentrations as shown. (**A**) Nitrogen-purged supporting electrolyte. (**B**) Oxygen-purged supporting electrolyte. Pressure 0.16 bar, scan rate 20 mV s^{-1}

Data for hydrogen peroxide concentration, as in Fig. 4, were obtained for all MGDE (0–10% AZO), and used for kinetic analysis. The reaction kinetics are not well defined for the first five minutes of electrolysis. Subsequently, the electrode inner channeling process completes, and the O_2 flow rate reaches a steady state. Provided there are no limitations to reactant mass transfer, hydrogen peroxide formation proceeds following a pseudo-zero-order kinetics with respect to oxygen concentration after five minutes of electrolysis. A zero-order rate law for a chemical reaction means that the rate of reaction is independent of the concentration of any reactant. A zero-order rate law can be observed only if the actual reactant concentrations cannot change as the reaction proceeds. As a gas diffusion electrode was used, concentration of oxygen is constant at the electrode surface once gas pressure is kept constant. Moreover, this consideration was also

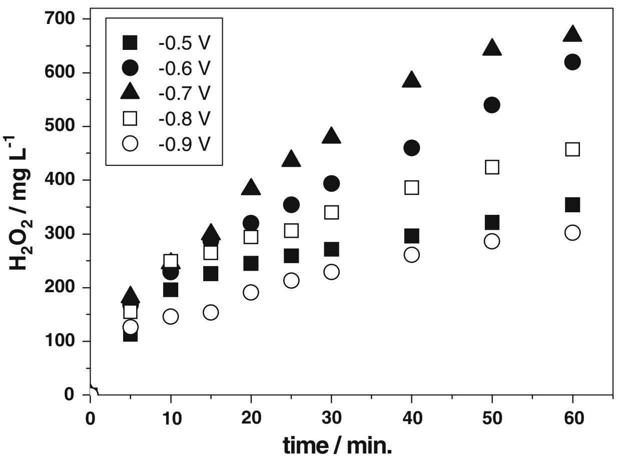


Fig. 4 H_2O_2 concentration as a function of electrolysis time for the MGDE containing 10% AZO. Supporting electrolyte: 0.1 M H_2SO_4 + 0.1 M K_2SO_4. O_2 pressure 0.16 bar

confirmed by the linear correlation between the concentration of H_2O_2 and the time of electrolysis.

Figure 5A shows values of pseudo-zero-order apparent rate constants (k_{app}) for hydrogen peroxide formation as a function of potential and compares the performance of electrodes containing different amounts of AZO. As a common feature all curves reach a maximum k_{app} value at –0.7 V vs. Ag/AgCl and decrease for higher potentials. The presence of AZO in the MGDE shifts the optimal potential by 300 mV less negative as compared to a non-catalyzed electrode, which has a maximum k_{app} value at –1.0 V vs. Ag/AgCl. This is an important number if scale-up of an electrolysis process is contemplated.

Figure 5B shows a plot of k_{app} values taken at –0.7 V vs. Ag/AgCl as a function of AZO concentration. The rising portion of the curve shows an increasing gain for the electrogeneration rate which is, however, attenuated from 5% of AZO, indicating 10% as an ideal AZO concentration.

After electrolysis, the final solution was analyzed by High Performance Liquid Chromatography (HPLC) (Shimadzu) using an online detection system with UV (λ = 365 nm). A CLC-ODS (M) column from Shimadzu was used, where an acetonitrile at a 1 ml min^{-1} flow rate was employed as eluent. The chromatograms were compared with a standard sample of azobenzene (140 ppm) dissolved in acetonitrile. The results showed that the azobenzene does not dissolve in the strongly acid medium employed.

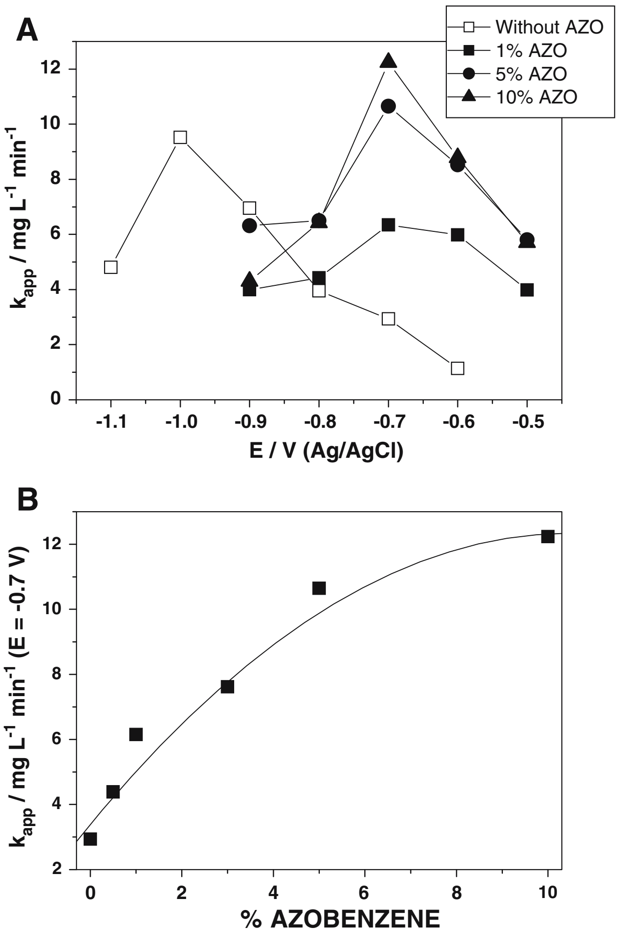


Fig. 5 (**A**) Apparent rate constants for H_2O_2 electrogeneration as a function of applied potential. (**B**) Apparent rate constants at –0.7 V vs. Ag/AgCl as a function of AZO concentration in the MGDE

4 Conclusions

This work has shown that the hydrogen peroxide formation rate on oxygen-fed graphite/PTFE may be greatly improved by the presence of an organic redox catalyst incorporated into the graphitic mass. Azobenzene, when used as catalyst, improved the H_2O_2 formation rate and reduced the overpotential for oxygen reduction by 300 mV less negative when compared to the performance of a non-catalyzed electrode. Moreover, these electrodes also show electroactivity in the reduction of hydrogen peroxide to water from –0.8 V vs. Ag/AgCl.

During electrolysis the hydrogen peroxide electrogeneration reaction exhibited pseudo-zero-order kinetics with respect to oxygen and apparent rate constants increased with azobenzene concentration.

On the basis of these results it is the intention of the authors to use such electrodes for large-scale hydrogen peroxide electrogeneration in a flow reactor.

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