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Electrosynthesis and properties of N,N dimethylaniline

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Poly-*N*,*N*-dimethylaniline was prepared by electrochemical polymerization of the monomer on gold, platinum and tin oxide electrodes in an acid medium. The polymer was characterized by cyclic voltammetry and scanning electron microscopy. Poly-*N*,*N*-dimethylaniline electrodes, modified by electrodeposition of palladium particles, were prepared.

1. Introduction

Organic polymeric deposits such as polypyrrole [1], polyacetylene [2], polythiophene [3] and polyaniline [4] have recently achieved a privileged position in the research field. They have been deposited on to electrode surfaces using various methods, e.g. electropolymerization [5], evaporation of a polymer solvent mixture [6], etc. The electropolymerization of some monomers is particularly attractive because the polymeric deposits exhibit some very interesting properties. They are generally homogeneous, strongly adherent to the electrode and chemically stable.

In the search for new conducting polymers of the aniline type, investigations have been directed towards anilines modified by substituents in the ring [7, 8] or at the nitrogen atom [9, 10]. This paper reports the preparation of poly-*N*,*N*-dimethylaniline (PDMA) film by anodic oxidation of *N*,*N*-dimethylaniline (DMA), and results of studies on its electrochemical properties and structure. Electrodes modified by the electrodeposition of small palladium particles within a polymeric matrix were also prepared.

2. Experimental procedure

The *N*,*N*-dimethylaniline was distilled under vacuum. The electrolyte was prepared using distilled water and reagent-grade sulphuric acid. After preparation, all solutions were deoxygenated with a stream of nitrogen within the cell, before and between experiments. The experiments were carried out at room temperature.

Electrochemical experiments were performed in a conventional cell with three electrodes. A saturated calomel electrode (SCE) was used as the reference electrode and all potentials were recorded and reported with respect to this electrode. The electropolymerization was carried out using cyclic voltammetry in 1 M H_2SO_4 and 0.1, 0.5 M *N*,*N*-dimethylaniline on gold, platinum and tin oxide electrodes. After electrodeposition, the poly-*N*,*N*-dimethylaniline was washed with the acid corresponding to the preparation medium.

Cyclic voltammograms and current–time (I–t) curves were recorded with a Brucker potentiostat (model E 310), Generator EG and G PAR (model 175) and a X–Y recorder (Hewlett–Packard model 7047A).

Scanning electron microscopy (SEM) was used to evaluate the morphology of the films. After electropolymerization some of the electrodes were placed in another three-electrode cell containing 5×10^{-2} M $PdCl_2$ and 1 M H_2SO_4 in distilled water. The electrodeposition of palladium was performed by applying potential and by cyclic voltammetry.

3. Results and discussion

The film was directly prepared on the working electrode (gold, platinum or tin oxide) by continuous potential cycling between -0.6 and 1.1 V/SCE in 0.5 M DMA and 1 M H_2SO_4 solutions at $V = 50\ \text{mV s}^{-1}$. A typical cyclic voltammogram of DMA solutions within this potential range is shown in Fig. 1. The observed anodic and cathodic peaks have been ascribed to the sequential one-electron oxidation

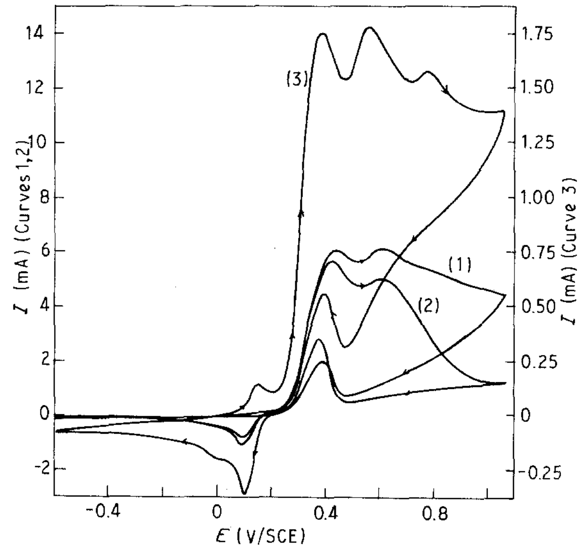

Figure 1 Cyclic voltammograms of 0.5 M DMA at a gold electrode in 1 M H_2SO_4. Scan rate $50\ \text{mV s}^{-1}$. Curves 1, 2 and 3 are for the first, second and third scans respectively.

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reactions. The anodic peaks at 0.4 and 0.6 V may correspond to the oxidation of DMA to the cation radical DMA^+ and then to the dication DMA^{2+}, respectively. The cathodic peaks are reductions of DMA^{2+} and DMA^+, although the peak currents are much smaller than the anodic one due to chemical reactions of the generated oxidized species. With successive potential scans, the anodic peak currents corresponding to the oxidation of DMA^+ and DMA^{2+}, decrease (Fig. 1, Curves 2 and 3), which can lead to the formation of the electroinactive polymeric films on the electrode surface. The electrode is covered with a uniform and insoluble adherent deposit. The film thus prepared is electrochemically homogeneous and shows great adherence to the surface of the base metal electrode (gold or platinum).

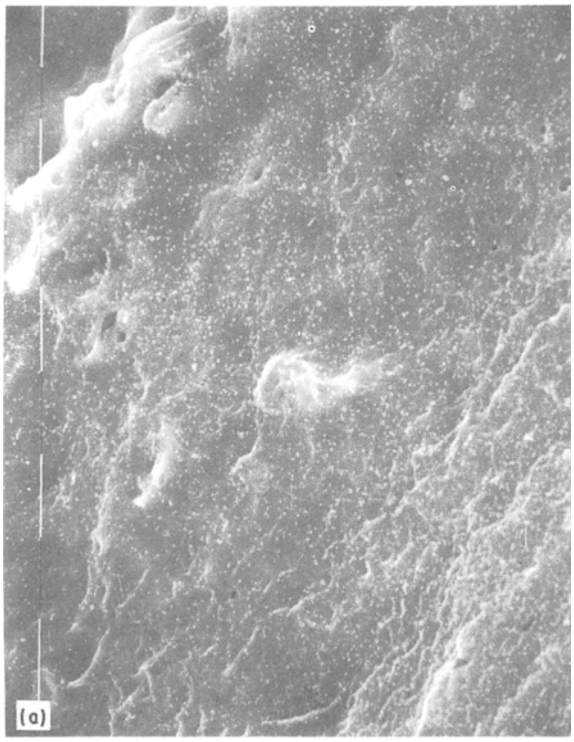
The last potential cycle was stopped at a potential of − 0.6 V. The film thus obtained was in the reduced state. The film-coated electrodes were washed with H_2SO_4 solution and with distilled water. When the substrate was gold or platinum the polymer had a similar aspect, but with tin oxide the polymer obtained was poorly adherent and very thin.

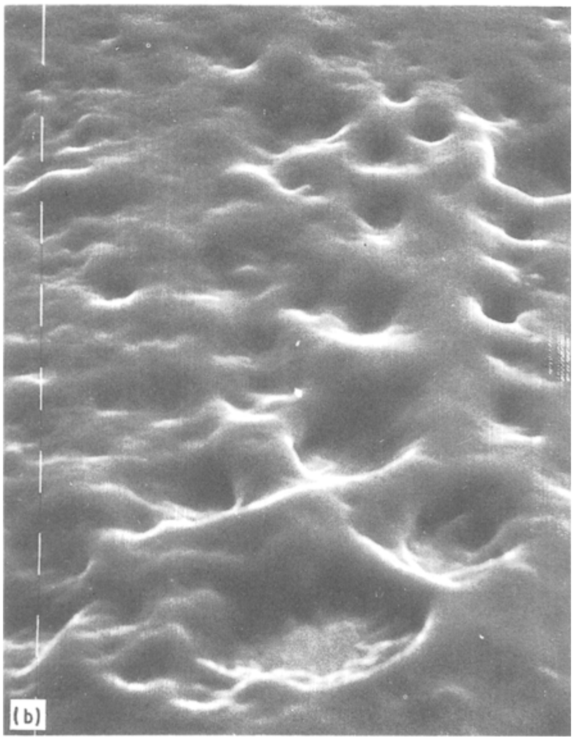
When the DMA concentration was 0.1 M in 1 M H_2SO_4, the behaviour was similar to the preceeding case (DMA 0.5 M), the current for the anodic peaks decrease with the successive potential scans and the value obtained for the intensity was approximately one-half, for gold and platinum substrates; for tin oxide apparently the polymer is not formed.

Several sets of potential step experiments were carried out, the potential was imposed from 0.0 V to values in the range from 0.4–1.5 V/SCE using 0.1 and 0.5 M DMA and 1 M H_2SO_4. The I–t transients were obtained. At potential values from 0.4–0.8 V a non-homogeneous and poorly adherent deposit was obtained.

The charging current with rising transient is attributable to a nucleation and growth mechanism. In the electropolymerization of DMA the nucleation process is not instantaneous. The slow nucleation causes a smooth and continuously increasing current but growth on the nucleus induces an increase in I–t producing an increase in the thickness of the polymer. The yellow–orange polymer is obtained on the gold and platinum electrode for $E > 0.8$ V/SCE, but for tin oxide the polymer thickness is poor and not very adherent. When the DMA concentration was 0.5 M the polymer obtained was thicker.

The microstructure of PDMA films prepared by the sweeping technique is shown in Fig. 2a and b. The film obtained had a slightly compact structure, and at a magnification of 1250 × for the same electrode deep valleys were seen. This polymer had a poor porosity.





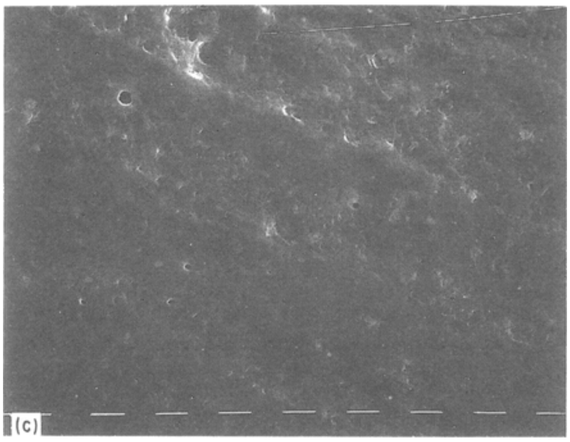


Figure 2 Scanning electron micrographs showing the morphologies of PDMA film grown in 1 M H_2SO_4 + 0.5 M DMA, (a, b) by cyclic voltammetry, 120 cycles on a gold electrode; × 640 and × 1250, respectively, and (c) at 0.85 V/SCE for 15 min on a gold electrode, × 640.

The microstructure of PDMA film prepared by the potentiostatic technique (Fig. 2c) ($E = 0.85$ V/SCE $t = 15$ min) did not have identical characteristics; this film shows less compact aspect than the previous case, and a smooth appearance is seen.

The cyclic voltammogram of PDMA (100 cycles with 0.5 M DMA) in 1 M H_2SO_4 at different sweep rates (V = 5–200 $mV s^{-1}$ (Fig. 3a), shows one main semi-reversible redox system that is quite stable to cycling if the switching potential is kept below 0.50 and − 0.2 V/SCE. When the anodic potential reaches values higher than 0.50 V, the electrode undergoes slow decomposition and the substrate, in this case gold, is exposed (Fig. 4). The destruction of the polymer is possible because of the irreversible deterioration of the film by formation of an electroinactive polymer film on the electrode surface. When the polymer was formed using potential steps, the electrochemical response in a blank solution is poor.

For different sweep rates (Fig. 3a) in solutions containing no monomeric DMA, the voltammograms are similar in appearance. Fig. 3b shows that the peak values of the current are linearly related to the square root of the sweep rate; this suggests a diffusion control of the oxidation process.

The electrocatalytic properties of modified electrodes prepared by electrochemical inclusion of metallic particles in a given polymer matrix depend on several factors, e.g. concentration of active centres, their size, and their spatial distribution. The Fig. 5

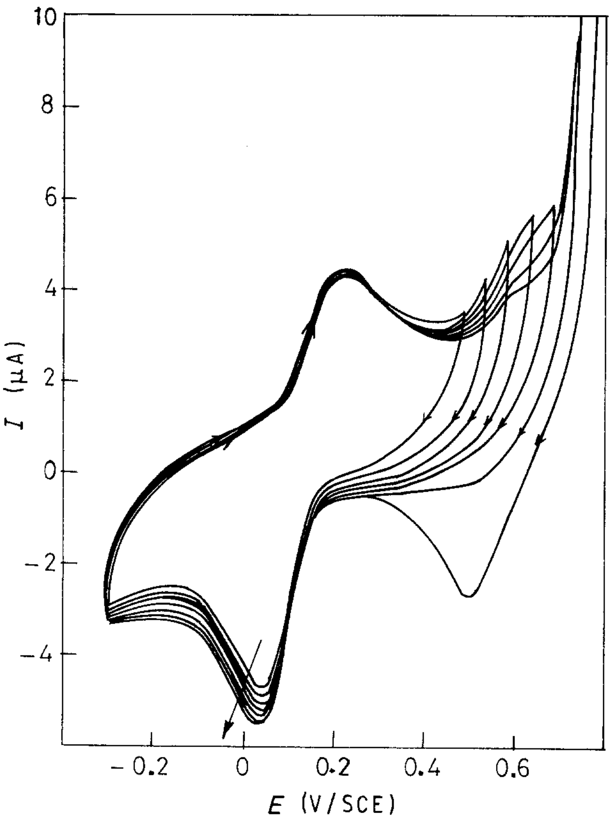


Figure 4 Influence of the positive potential limit on the voltammogram of PDMA in 1 M H_2SO_4, 25°C and 50 $mV s^{-1}$.

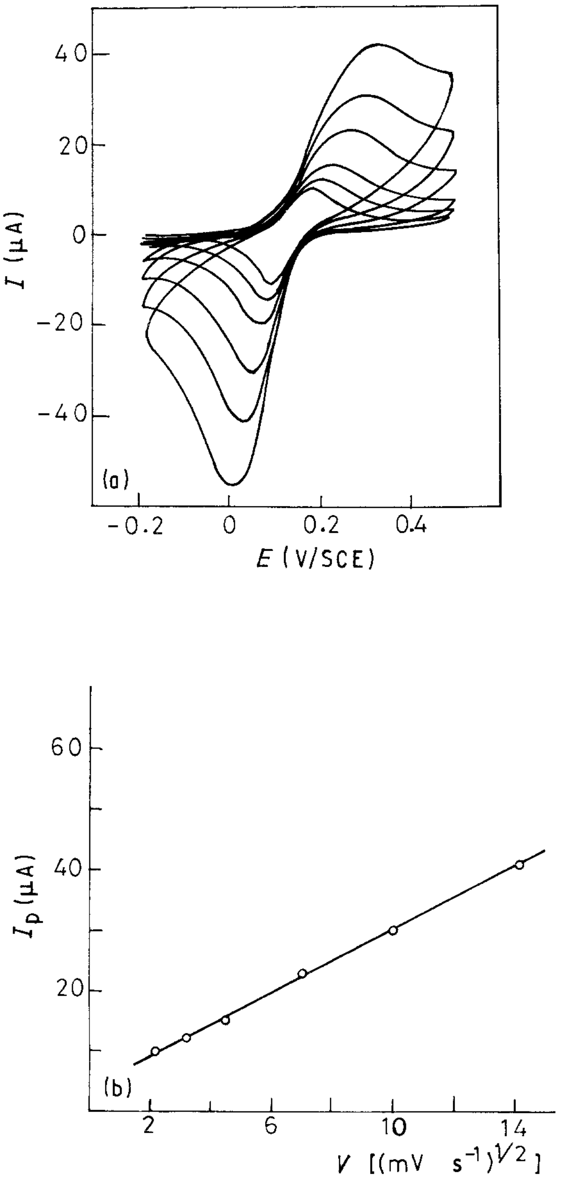


Figure 3 (a) Cyclic voltammograms showing the electroactivity of PDMA film on a gold substrate at different scan rates: 5, 10, 20, 50, 100 and 200 $mV s^{-1}$ in 1 M H_2SO_4. (b) Variation of the anodic peak current intensity as a function of scan rate.

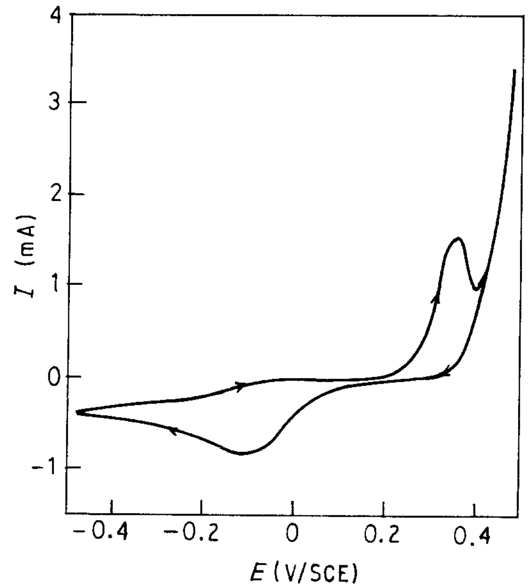


Figure 5 The cyclic voltammograms of PDMA electrode in 0.05 M $PdCl_2$ and 1 M H_2SO_4, 25°C and $V = 50$ $mV s^{-1}$.

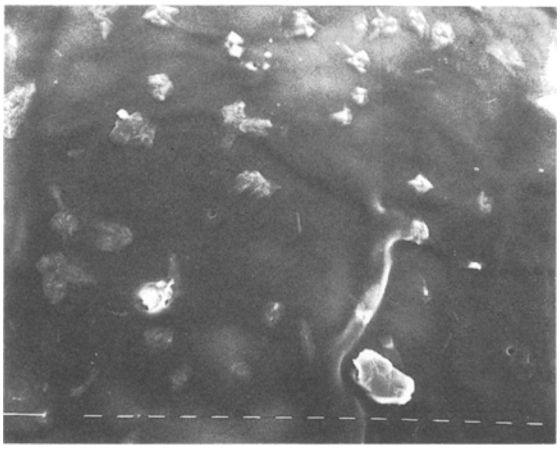


Figure 6 Scanning electron micrographs of palladium particles included in a PDMA deposit prepared in 0.05 M $PdCl_2$ and 1 M H_2SO_4 E_{dep} − 0.3 V during 60 s on a gold electrode (× 320).

shows the current–potential curve corresponding to the electrodeposition of palladium in PDMA film in an aqueous solution containing 5×10^{-2} M $PdCl_2$ and 1 M H_2SO_4. This polymer was washed and the palladium PDMA-modified electrode was studied in 1 M H_2SO_4. The voltammogram shows a broad hydrogen adsorption wave.

The palladium was deposited at $E = -0.3$ V, $t = 60$ s in 5×10^{-2} M $PdCl_2$ and 1 M H_2SO_4. This Pd/PDMA electrode was tested in blank solution of 1 M H_2SO_4. In the presence of deposited palladium the coupled peak of the polymer is inhibited and a well-defined hydrogen adsorption wave is obtained.

Fig. 6 shows a scanning electron micrograph of palladium microparticles deposited at $E = -0.3$ V/SCE, $t = 60$ s. The metal deposition appears to be very heterogeneous, deposition being predominantly on the external surface of the PDMA electrode. The palladium particles were spherical, had a large variation in apparent particle size, and were distributed along the polymer. This indicates that there may be preferential sites for nucleation and subsequent growth through the polymer film. The microparticles, which are formed by initial nucleation at the polymer/substrate interface, provide sites for further charge transfer, resulting in continued growth of the metal particles through the polymer films. This is not surprising, considering the nonconducting nature or poor conductivity and the hydrophylic character of the polymer film in this potential region.

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