



Conductive organic polymers: An electrochemical route for the polymerization of dapsone



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ABSTRACT

The electropolymerization of dapsone by anodic oxidation is reported for the first time. The conditions in which a non-conducting oligomeric film or a conductive polymeric film of dapsone is formed are also discussed, based on the scan rate and potential window applied. The cyclic voltammetry of dapsone-polymer presented redox activities that have not been shown before, to the authors' knowledge, demonstrating its high electronic conductivity. The electrochemical impedance response of the dapsone-polymer indicates that their admittance is similar to pure and sulfonated polyanilines, while for the dapsone-oligomers is characteristic of insulating materials. Infrared spectroscopy of both oligomers and polymer supports that the polymerization occurs via amino–amino coupling, since no modifications in the aromatic ring is observed.

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1. Introduction

Polymers from the polyaniline family are considered the most promising conducting organic materials, due to their environmental stability and reversible acid/base doping/dedoping characteristics [1]. Polydapsone belongs to this family, and the first report found on its synthesis is attributed to Dan and Sengupta [2], who prepared the polymer through a chemical oxidative method. Thereafter, conductive copolymers of dapsone with aniline [3], pyrrole [4], diphenylamine [5], and 4-aminodiphenylamine [6] have been prepared through chemical and electrochemical methods, showing electroactivity. Spectroelectrochemical studies of these copolymers deposited as films over indium–tin oxide (ITO) plates showed a varying multicolor electrochromic behavior with the applied potential.

Manisankar and co-workers [7] have conducted electrochemical studies on dapsone (Fig. 1), performing cyclic voltammetry in dapsone solutions with different pH values (1 to 13) and in a wide range of potential window (–0.9 to 2.5 V) and scan rates (0.10 to 1.00 V s^{–1}). In such conditions, they showed that dapsone undergoes an irreversible

oxidation process in the potential range of 1.1 to 1.9 V using Ag/AgCl reference electrode, and they attributed the current signal loss after the first anodic scan to the homopolymerization of dapsone [5,6,8], with the resulting formation of a low conductive film.

Nonetheless, non-conducting films are typically formed by a few units of impermeable dimers or oligomers, subsequently producing few electroactive sites [9,10], such as in the dimerization of aniline [11–13], phenol [14–16] and quinones [17–19]. In this letter, we report the successful electrochemical synthesis of a conductive dapsone polymer using cyclic voltammetry in a lower potential window and high scan rates. It is also shown that applying a higher potential window leads to forming impermeable dapsone dimers and/or oligomers, subsequently blocking the glassy carbon electrode (GCE).

2. Experimental

2.1. Chemicals

Dapsone, ethanol, sulfuric acid, potassium chloride and sodium hydroxide were purchased from Sigma–Aldrich and used as received. The supporting electrolyte solutions were prepared as follow; H₂SO₄ in 50% (v/v) aqueous alcohol (pH 1.0 to 3.0), 0.1 mol L^{–1} KCl in 50% (v/v) aqueous alcohol (pH 4.0 to 7.0), 0.1 mol L^{–1} NaOH in 50% (v/v) aqueous alcohol (pH 8.0 to 14.0). Ultrapure water (Millipore® System, resistivity 18.2 MΩ cm) was used throughout the experiments.

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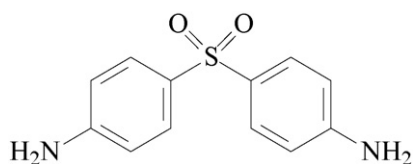


Fig. 1. Structure of dapsona.

2.2. Electrochemical measurements

All electrochemical experiments were performed using an AUTOLAB PGSTAT302N potentiostat/galvanostat electrochemical analyzer. A stationary GCE (BAS Model MF 2012; geometric area = 0.0774 cm²), a Ag/AgCl/KCl(satd.) reference electrode, a platinum counter electrode (geometric area = 1.0 cm²) and a standard one-compartment three-electrode cell (15 mL capacity) were used in all experiments.

Electropolymerization was carried out by cyclic voltammetry using 5.0 mmol L⁻¹ dapsona in an aqueous ethanol (50%, v/v) solution containing H₂SO₄ (pH 1.0) as supporting electrolyte. The electrode surface was cleaned before each experiment by mechanical polishing over a velvet micro-cloth embedded with an alumina suspension (0.3 μm) and by an electrochemical treatment, applying a potential of +1.5 V for 4 s, in the same supporting electrolyte used in the electropolymerization. The immobilized films on GCE and indium-tin oxide (ITO, resistivity <7.0 Ω cm, transmittance >77%) were obtained by applying fifty cyclic potentials in potential window from 0.00 to 1.02 V. We evaluated the influence of the scan rate for obtaining films in the range of 0.01 to 1.00 V s⁻¹. After the 50th cycle, the GCE-modified obtained at 1.00 V s⁻¹ was washed with ultrapure water and transferred to another electrochemical cell containing only the supporting electrolyte (free of dapsona) at various pH, and subjected to cyclic voltammetry within the potential window of -0.10 to 0.80 V and scan rates from 0.025 to 1.00 V s⁻¹. In addition, the stability of the film immobilized on GCE (the polymer) was tested by carrying out 1000 potential cycles within -0.10 to 0.80 V at a scan rate of 1.00 V s⁻¹. The polymer and oligomers activity was qualitatively evaluated by the Fe³⁺/Fe²⁺ system in a cell containing a 5.0 mmol L⁻¹ K₃[Fe(CN)₆] and 1.0 mol L⁻¹ KNO₃ aqueous solution (pH 6.5). At last, electrochemical impedance spectroscopy was carried out at a temperature of 298 K in a Faraday cage to avoid external electromagnetic interference. The impedance measurements of the polymer and oligomers were done at open circuit potential (OCP) with applied 10 mV RMS sinusoidal AC perturbation in the frequency range of 10⁻² to 10⁵ Hz with 10 data points per decade, using an aqueous ethanol (50%, v/v) solution containing H₂SO₄ (pH 1.0) as supporting electrolyte.

The impedance plots were fitted using commercially available NOVA 1.11 (Autolab) software.

2.3. Infrared spectroscopy measurements

The spectral changes in vibrational bands of the oligomeric and polymeric films produced over ITO electrode were analyzed by UATR-FTIR (Universal Attenuated Total Internal Reflection Fourier Transform Infrared) spectroscopy recorded using a Spectrum One Perkin Elmer spectrometer, under the following conditions: 4000 to 780 cm⁻¹, 20 scans and a resolution of 4 cm⁻¹. ITO-coated electrodes with oligomeric and polymeric films were placed on the Zn–Se crystal and a pressure of 100 N was applied to ensure a good contact between sample and crystal, preventing loss of infrared radiation.

3. Results and discussion

3.1. Electrochemistry

Fig. 2a shows, the first three and the 50th cycle from the cyclic voltammetry obtained at 1.00 V s⁻¹ scan rate and 0.00 to 1.02 V potential window. In the first forward anodic scan, no faradaic process is observed up to 0.8 V; above this potential, the oxidation of dapsona takes place and the nucleation and maximum growth of the polymer occurs up to 1.02 V, which corresponds to the oxidation peak. In the first reverse scan, the appearance of cathodic current peaks is evident at around 0.72, 0.52 and 0.13 V, which we denoted as C₁, C₂ and C₃, respectively. From the second cycle on, three anodic current peaks arise at 0.41, 0.55 and 0.75 V, denoted as A₁, A₂, and A₃, respectively. The progressive increase in the current of these peaks (verified at least up to the 50th cycle), suggests the continuous formation of polydapsona film over the GCE surface.

Fig. 2b shows the 50th cycle of the cyclic voltammogram (CV) for each scan rate evaluated from 0.01 to 1.00 V s⁻¹ and 0.00 to 1.02 V potential window. To avoid unpredictable responses from the electrode the GCE surface was cleaned between each scan rate step, as mentioned in the Experimental section. From Fig. 2b it can be observed that the current peaks show no significant intensities below a scan rate of 0.10 V s⁻¹. Thusly, we conclude that high scan rates are needed for the faster incorporation of monomeric dapsona into the oligomeric chains, in order to form polydapsona. Fig. 2b inset shows that there is a linear relationship between the peak currents (C₂, C₃, A₁ and A₂) and the scan rate, indicating that the process is limited by charge transport and not by diffusion, as expected for surface-modified electrodes [9,10].

Dapsona polymer is assumably formed by -N-N- bonds (see Section 3.2), and the resonance process in the cation radical formed

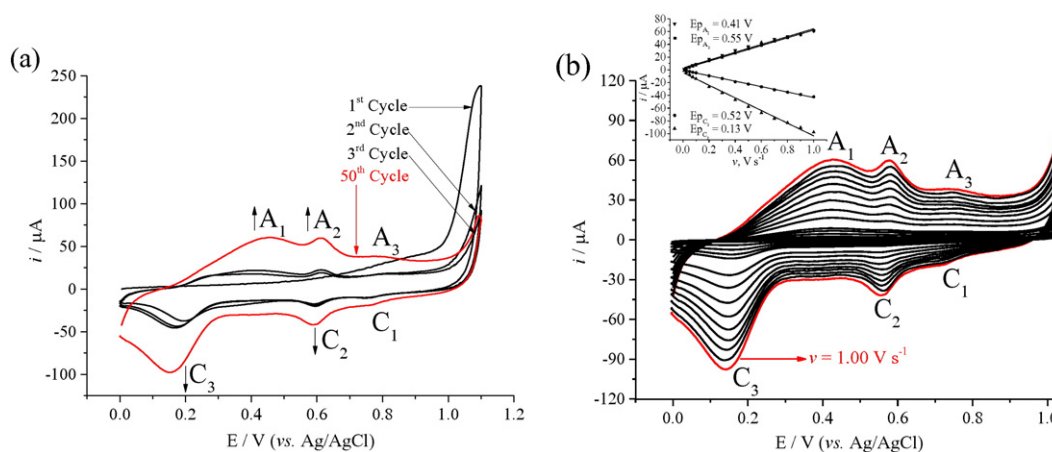


Fig. 2. Influence of scan rate on the kinetics of electropolymerization of dapsona. (a) CV at a fixed scan rate (1.00 V s⁻¹); (b) 50th CV for each scan rate cycle (from 0.01 to 1.00 V s⁻¹). Supporting electrolyte: aqueous ethanol (50%, v/v) solution containing H₂SO₄ (pH 1.0).

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