



# Galvanodynamic synthesis of polyaniline: A flexible method for the deposition of electroactive materials



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## ABSTRACT

Galvanodynamic synthesis is introduced as a new flexible electrochemical method for the preparation of electroactive materials, as utilized for electropolymerization of aniline in the present seminal work. It is indeed a missing method in the four possible electrochemical methods namely potentiodynamic, potentiostatic, galvanostatic, and finally galvanodynamic. This explicit comparative study shows the flexibility of this method in controlling the physical and electrochemical properties of the polyaniline film. Electrochemical polymerization was performed by scanning the current in a given range. Different approaches for this purpose were also introduced as the synthesis can be performed under different conditions through linear scanning, cyclic scanning, and repetitive cyclic scanning. Effects of various controllable parameters, such as scan rate, the current range, and the scan direction were also examined. In comparison with other electrochemical methods, galvanodynamic synthesis has higher flexibility to alter controllable parameters in favor of a specific application. For instance, synthesis of polyaniline to display characteristic redox peaks suitable for battery performance or strong capacitive behavior ideal for supercapacitors.

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## 1. Introduction

Since the first report of electropolymerization by Diaz et al. [1], this is one of the dominant approaches for the synthesis of conductive polymers. Different electrochemical techniques such as potentiodynamic [2–10], potentiostatic [11–19], and galvanostatic [20–29] have been successfully employed for electropolymerization of monomers. The first one is based on cyclic voltammetry, which is a common electrochemical technique. In this method, electropolymerization is performed by scanning the potential in a given potential range covering the potential required for the monomer oxidation and the polymer growth. The second one is performed by applying a constant potential to polymerize the monomer. The third one is based on applying a constant current. In general, all three methods are based on applying the required current or potential to initiate the electropolymerization process. However, the results are quite different, and it is indeed an important factor for the investigation of conductive polymers (and mechanism of polymerization), and more importantly provides unique opportunities for the preparation of desirable conductive polymers [30–43].

In these electrochemical methods, the applied current or potential can be constant or under scanning condition. This reminds that another method is missed in this variety, as the current can also be scanned. Similar to the case of potentiodynamic polymerization, it is named galvanodynamic polymerization. The latter method could be also employed for the electrochemical synthesis of conductive polymers, but to our knowledge, there is no report utilizing this method. This can be attributed to the fact that galvanodynamic method, *i.e.*, voltammetry under galvanostatic condition, is not a common electrochemical technique. However, it is very simple and can be performed by almost all modern electrochemical instruments.

Since the main theme of the present paper is to introduce a new method for the synthesis of conductive polymers, the results were reported in a comparative manner to reveal the role of controllable factors. In a systematic research, voltammetric behavior and morphology of each polyaniline film is reported, as they are common properties of electroactive materials including conductive polymers. On the other hand, this introduces an opportunity for design of co-electrodeposition leading to the formation of polymer-based (nano)composite films, which is indeed an active area of both fundamental and applied research [44].

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## 2. Experimental

All electrochemical experiments including galvanodynamic synthesis were performed using an Autolab PGSTAT30 potentiostat/galvanostat connected to a computer running its corresponding software. The electrochemical polymerization of aniline was carried out from a typical electrolyte solution of 0.1 M aniline in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The current scan rate was typically 200  $\mu\text{A cm}^{-2} \text{s}^{-1}$ , unless otherwise noted for the investigation of the influence of scan rate. The working electrode was a Pt plate prepared from a thick platinum foil (with thickness 0.5 mm) to facilitate the SEM investigations. One side of the foil was insulated to guarantee the common one-dimensional electrochemistry. A conventional three-electrode cell containing a Pt rod as the counter electrode and an Ag/AgCl in 3 M KCl as the reference electrode was employed for the electrochemical measurements. Different polyaniline films were synthesized by this method according to the experimental conditions specified in the text. After the electropolymerization process, the polyaniline films were thoroughly washed with double distilled water and dried at 60 °C.

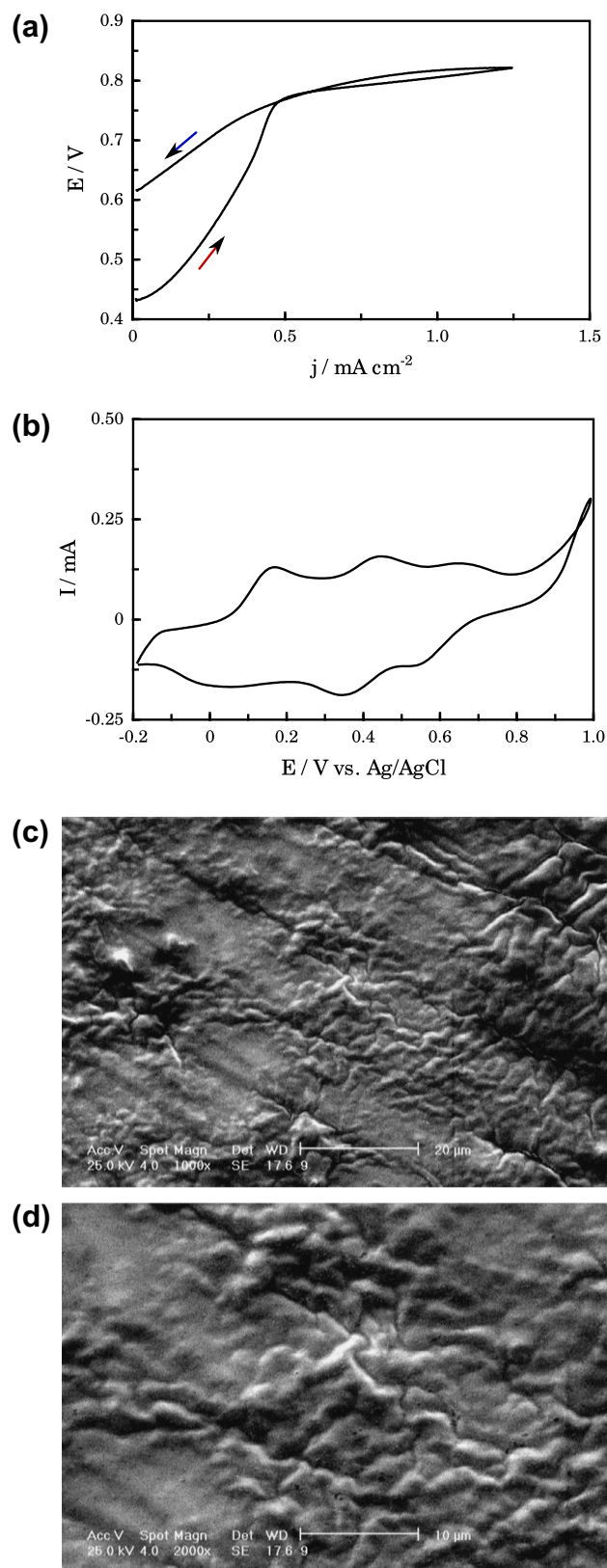
The cyclic voltammetric measurements were also carried out with the same apparatus in the supporting electrolyte of 0.5 M H<sub>2</sub>SO<sub>4</sub>, and the potential scan rate was typically 100  $\text{mV s}^{-1}$ . SEM images were taken by a Philips XL30 scanning electron microscope.

## 3. Results and discussion

Fig. 1a shows a galvanodynamic synthesis of polyaniline performed in the course of a complete cycle with the upper limit of 1.25  $\text{mA cm}^{-2}$ . Similar to the conventional galvanostatic synthesis of conductive polymers, the potential can be representative of the electropolymerization process. For the current densities lower than 0.5  $\text{mA cm}^{-2}$ , the potential is low to initiate the electropolymerization process. It is in agreement with the galvanostatic synthesis of conductive polymers, as no electropolymerization occurs at low current densities. For the typical case of polyaniline, galvanostatic polymerization just occurs at current densities higher than 0.5  $\text{mA cm}^{-2}$ , which is in full agreement with the results obtained here for galvanodynamic polymerization.

By scanning the current from 0 to 0.5  $\text{mA cm}^{-2}$ , the potential monotonically increases to reach the value of 0.8 V vs. Ag/AgCl, which is sufficient to induce the electropolymerization of aniline. After reaching this value, the potential is approximately constant for higher values of the current density (e.g., up to 1.25  $\text{mA cm}^{-2}$ ). In the latter regime, the electropolymerization of aniline occurs but it is different across the current scanning. During the reverse scan, the electropolymerization proceeds in the same manner, but for the current densities lower than 0.5  $\text{mA cm}^{-2}$ , the first regime is not similar to that observed during the forward scan. This can be attributed to the fact that electropolymerization of aniline on previously deposited polyaniline (i.e. continuing the polymer growth) is easier than that on the bare substrate surface. Thus, electropolymerization occurs even at low current densities in the course of reverse scan.

After galvanodynamic synthesis of polyaniline according to the simple manner followed above, it is necessary to examine the electrochemical behavior of this polyaniline film. Fig. 1b shows a characteristic voltammetric behavior of polyaniline having three redox couples. In fact, the polyaniline film synthesized by galvanodynamic method displays an ideal electrochemical behavior as well as those synthesized by other electrochemical techniques. Since, in galvanostatic synthesis of conductive polymers, the applied current density strongly affects the film morphology, it is appropriate to examine this feature for the system under investigation. SEM images of the polyaniline film prepared in Fig. 1a



**Fig. 1.** (a) Cyclic galvanodynamic polymerization of aniline with the current scan rate of 200  $\mu\text{A cm}^{-2} \text{s}^{-1}$ , and (b) cyclic voltammetric behavior of the resulting polyaniline film in the supporting electrolyte of 0.5 M H<sub>2</sub>SO<sub>4</sub> recorded with the potential scan rate of 100  $\text{mV s}^{-1}$ . (c and d) SEM images of the polyaniline film.

illustrate a smooth but wrinkled surface (Fig. 1c and d). This is of particular interest, as this morphological structure is not common

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