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Effect of thickness on the electrochemical behavior of the polyaniline film

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Introduction

The electrochemical behavior of PANI film is mainly arisen from the redox reaction along with the doping process. In this regard, the film thickness is an effective parameter [1-4] . It is believed that for a thin PANI film < 500 nm doping process is not only due to the ion incorporated into the film but also due to the ions placed adjacent to the film surface [5]. Moreover, for a thin PANI film with a thickness less than150 nm, the mass transfer through the film is not significant [4]. The aim of this work is to experimentally investigate the effect of thickness on the electrochemical behavior of PANI film.

Methods

PANI films were made by the electropolymerization method on the surface of a gold electrode (1 cm^2) in a conventional three electrodes cell. To obtain films with different thickness, the amount of charge passed during electropolymerization (Q_p) was changed according to that presented in Table 1. The obtained PANI film was immersed in 1 M HCl and the cyclic voltammetry (CV) was conducted between -0.2 and 0.4 V at the potential scan rate of 10 mV s^{-1}.

Results and discussion

The thickness of PANI films was estimated according to equation suggested in [2, 3] and reported in table 1.

Table 1 The estimated thickness for PANI films electropolymerized with different Q_p

Q_p (mC cm^{-2})	7	14	22	29
Estimated thickness (nm)	22	46	72	95

the number of electroactive sites (Γ) presented in each film was calculated as follows [6, 7]:

$$\Gamma = \frac{Q}{n\mathrm{F}} \quad (1)$$

where Q (C cm^{-2}) represents the amount of charge passed in oxidation peak, n the number of exchange electron for redox reaction and F the Faraday constant. The variation of Γ versus film thickness and oxidation peak current ($I_{p,Ox}$) versus Γ are shown in Fig. 1. It is obvious that there is a linear relation between Γ and film thickness (Fig. 1 a) and also a similar relation exists between $I_{p,Ox}$ and Γ (Fig. 1 b). The latter evidence represents the behavior of adsorbed electroactive sites [8, 9]. Moreover, the CV data showed that the increase of Γ has no significant effect on the peak potentials ($E_{p,Ox}$) (not shown here) and hence on the feasibility of redox reaction and doping process.

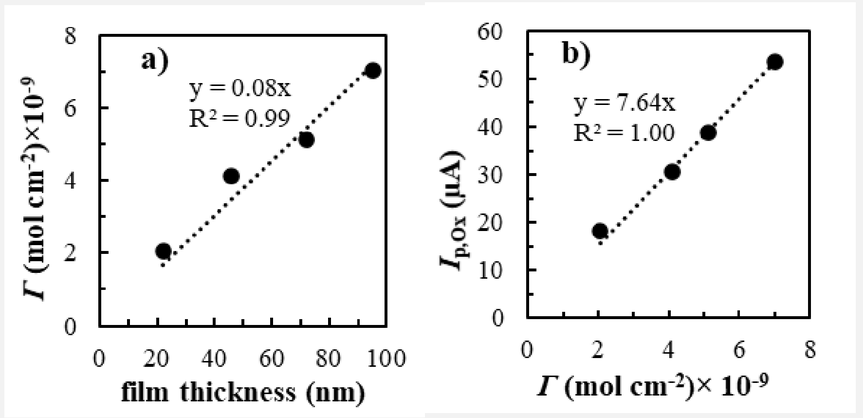

Fig. 1 The variation of the number of active sites with film thickness and its' effect on the peak current

Conclusion

In this work, it was observed that the increase of PANI film thickness increases the number of electroactive sites and has a linear relation with the $I_{p,Ox}$. This linearity indicates that the electrochemical behavior of PANI film is as the adsorbed electroactive sites. Furthermore, the value of $E_{p,Ox}$, which is a sign of the reaction feasibility, remains almost constant. Therefore, for a thin PANI film, in the thickness range of the present work, , the increase of film thickness affects only on the number of active sites and not on the feasibility of redox reaction and doping process.

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