

# Electrocatalytic Properties of Platinum Doped Polyaniline and Polypyrrole Electrodes

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This review paper aims to show how the electrochemical behaviour of polyaniline (PANI) and polypyrrole (PPy) electrodes modified by platinum help to improve the oxidation of organic molecules such as methanol, ethylene glycol and glucose. Although the amount of platinum deposited was very small, i.e.,  $0.1 \text{ mg.cm}^{-2}$ , the catalytic activity obtained was comparable to bulk platinum. Another notable point is the reduction of the poisoning effect, which is the main problem faced in the electrooxidation of organic molecules for fuel cell applications.

## Introduction

Polymer films, known as polymer modified electrodes, with metal particles incorporated into the film either during film formation or by electrodeposition onto the polymer films, were found to be good catalysts for certain electrochemical reactions of importance for application in fuel cells<sup>1</sup>. In particular, the use of platinum particles seems to be very advantageous. When platinum is deposited electrochemically, the particles are distributed three dimensionally in the layer due to the porosity of the polymer. Among the polymer films, polyaniline and polypyrrole have certain advantages over other conducting polymers, including simplicity and rapidity of preparation by electrochemical methods, chemical durability against aerial oxidation, and the ability to be formed in aqueous electrolytic solutions<sup>2-7</sup>.

In the present study, electrooxidation of methanol, ethylene glycol and D-glucose is reviewed as function of deposition potential of platinum. Effect of the temperature and concentration of the organic molecules are also investigated.

## Experimental

PANI and PPy films were deposited on a Pt foil by electrochemical techniques. Polymerization of aniline was achieved from solutions containing 0.1 M aniline in 0.5 M H<sub>2</sub>SO<sub>4</sub> by sweeping the potential continuously between -0.6 and +0.4 V/MSE until a film of certain thickness was obtained. Film thickness was determined using the charge value of the first anodic peak of the last growth cycle during PANI film formation. A charge value of 40 mC.cm<sup>-2</sup> has been reported to correspond to a 0.6 μm-thick film<sup>8</sup>.

PPy films were deposited by electrolysis at a constant potential (+0.43 V/MSE). The thickness of the polymer layer was estimated as 0.2 μm<sup>7,9</sup>.

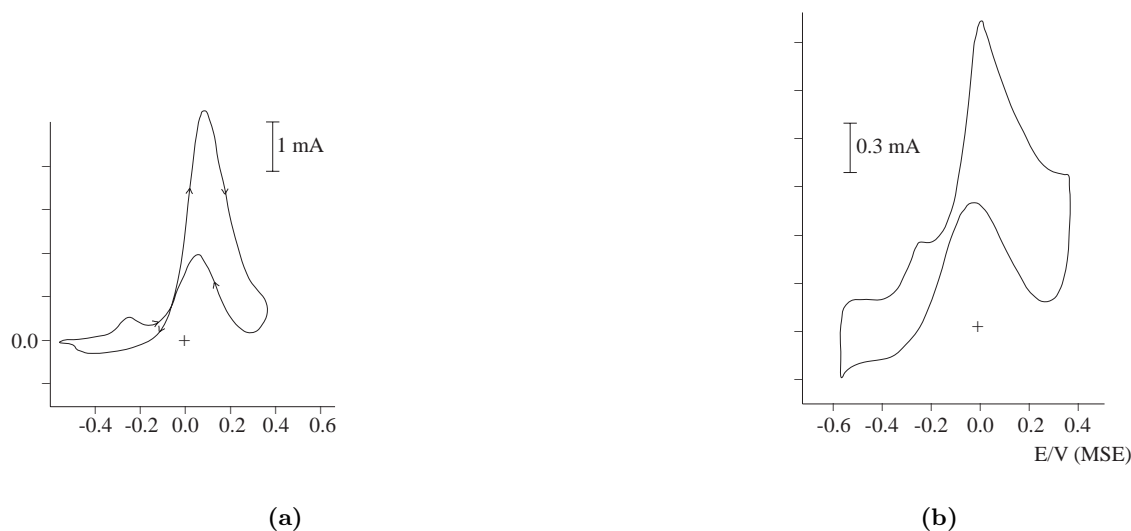
Platinum particles were incorporated by electrochemical deposition from a solution containing 0.01 wt% hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) at constant potentials in 0.5M H<sub>2</sub>SO<sub>4</sub> solution in the case of PANI substrate, and in phosphate buffered solution (pH=6.8) in the case of PPy electrode.

All experiments were performed using the electrochemical equipment and electrolytic solutions mentioned previously<sup>10-11</sup>. A mercury-mercurous sulphate electrode (MSE) was used as the reference.

## Results

### Electrocatalytic properties of the platinum doped polyaniline electrode:

The experiments were carried of by varying the deposition potential at a constant platinum loading of 100 μg.cm<sup>-2</sup> for methanol and 150 μg.cm<sup>-2</sup> for ethylene glycol oxidation. A voltamogram of methanol and ethylene glycol oxidation on an electrode formed in such a way is given Fig. 1.



**Figure 1.** Electrooxidation of organic molecules on PANI-Pt electrode, 0.5M H<sub>2</sub>SO<sub>4</sub>,  $v = 10 \text{ mVs}^{-1}$ ,  $t = 25^\circ \text{C}$   
 a) 0.1M methanol b) 0.1M ethylene glycol

Voltammetric curves show that the oxidation of methanol and ethylene glycol on platinum modified PANI starts on the potentials corresponding to the double layer region of platinum (at -0.1 V). The oxidation rate increases at more positive potentials, reaching a maximum at about 0.1 V.

During the reverse scan, the electrode sites were almost blocked by the surface oxide layer until it began reduction, so that the methanol and ethylene glycol oxidation started again, reaching a weak current peak. The positive and negative potential scans were not superimposed because of the different intensities; however, the shift of peak potentials was not significant, i.e., the strongly chemisorbed poisoning species were not formed to a great extent on the modified PANI electrode.

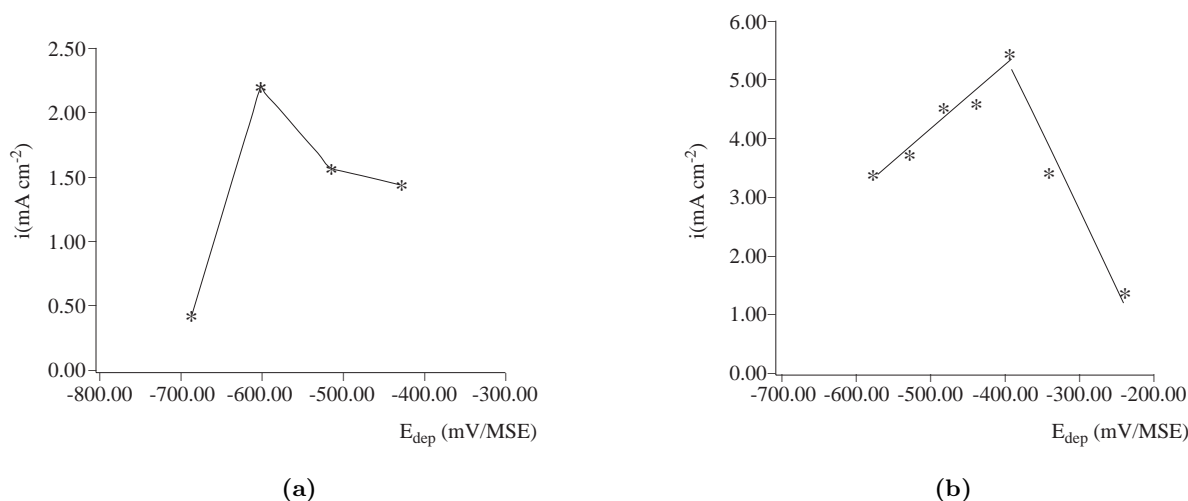
Effects of platinum deposition potential on the electrooxidation of methanol and ethylene glycol were tested by recording the corresponding cyclic voltammogram after each deposition process in a solution containing 0.1M methanol or ethylene glycol in 0.5M  $H_2SO_4$  with a sweep rate of  $10\text{ mVs}^{-1}$  (Fig. 2). Catalytic activities were compared using the intensity of anodic peak of methanol or ethylene glycol. Maximum current densities were obtained for  $E_{dep} = -0.365\text{V}$  in the case of methanol and  $E_{dep} = -0.565\text{V}$  in the case of ethylene glycol oxidation.

### Electrocatalytic properties of the platinum-doped polypyrrole electrode:

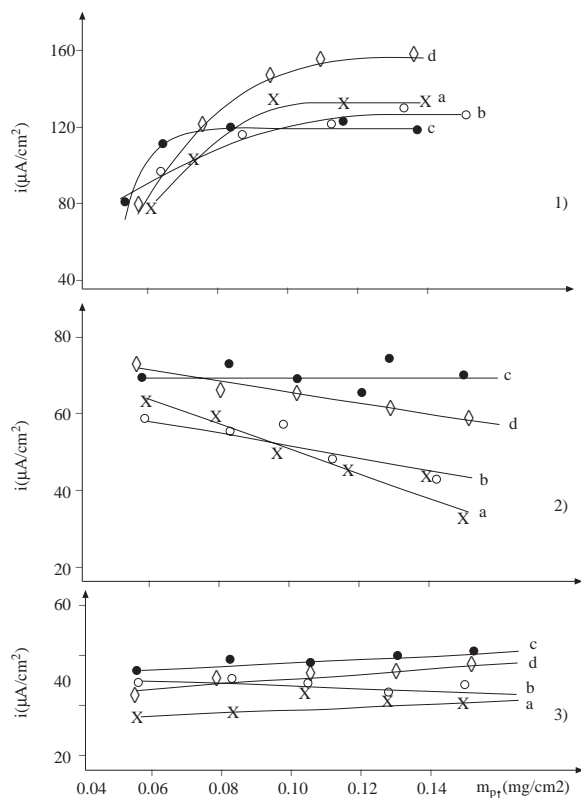
Experiments were performed mainly in a neutral medium at  $\text{pH} = 6.8$ . Phosphate buffer solutions ( $0.1\text{M Na}_2\text{HPO}_4 + 0.1\text{M KH}_2\text{PO}_4$ ) were used to maintain the neutral medium. According to our previous study<sup>11</sup>, minimum platinum loading to obtain higher activity than pure platinum was found to be  $65\text{-}100\ \mu\text{g.cm}^{-2}$ . With the platinum loading kept constant at  $65\ \mu\text{g.cm}^{-2}$ , the deposition potential of platinum was varied. Maximum current density was obtained for  $E_{dep} = -0.56\text{V}$  (Fig. 3).

Fig. 4 shows the voltammograms of 0.1M D-glucose both on pure platinum and platinum-doped polypyrrole electrodes in a phosphate-buffered solution at  $25^\circ\text{C}$ . Three oxidation peaks obtained on pure platinum were also seen on the modified electrode. While the oxidation of peak A was observed at more negative potentials, oxidations at peaks B and C shifted towards more positive potentials than those seen on the platinum electrode. Peak densities were also more intense.

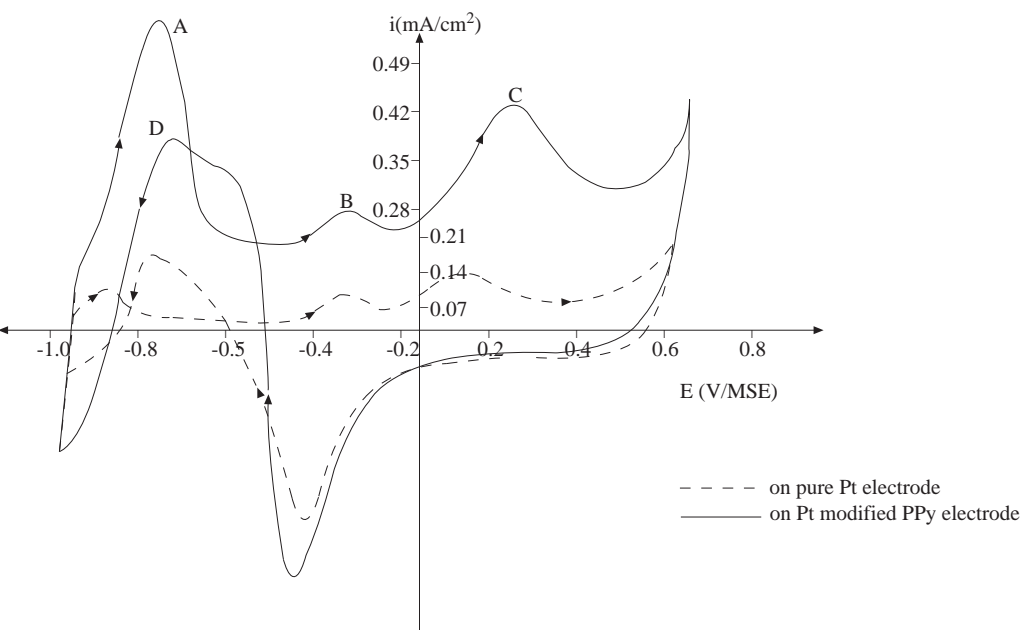
Overall reaction order was determined for D-glucose oxidation on modified electrodes by varying the concentration. The calculated reaction order was about 1 for peaks A and D. As an approximation, one can assume that the rate-determining step depends on the initial concentration of glucose.



**Figure 2.** Deposition potential of Pt vs. maximum current density plot for the determination of optimum deposition potential a) for 0.1M ethylene glycol b) for 0.1M methanol



**Figure 3.** Pt loading versus max current density of D.glucose oxidation at 0,1M phosphate buffer after the modification by platinum at applying following potential values. a) -0.36 V/MSE b) -0.46 V/MSE, c) -0.56 V/MSE d) -0.66 V/MSE 1) Peak A 2) Peak B 3) Peak C



**Figure 4.** Electrooxidation of D.glucose in 0.1M phosphate buffer,  $v = 50 \text{ mVs}^{-1}$ ,  $t = 25^\circ\text{C}$ .

## Conclusion

The results show the importance of the deposition potential of platinum both on PANI and PPy electrodes during for the oxidation of organic molecules. An increase in the maximum current density was obtained by changing the deposition potential of platinum on polymer films. Electrochemical deposition potential may offer control over the properties of crystalline structure and grain morphology of the platinum on the surface. Hence, the electrical and catalytic properties of the surface may change. An increase in the peak densities on modified electrodes relative to pure platinum may be explained by the decrease of strongly chemisorbed species. This may be due to an arrangement of active sites required by strongly chemisorbed species on the catalyst surface, which is not provided by the platinum deposition conditions on polymer electrodes.

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## FOREWORD

There are now number of research groups working with electroactive polymers in Turkey hence the idea of a workshop with some participation outside of Turkey was discussed during the brief conversation between myself and Prof. Zerbi at the 209th ACS National Meeting in Anaheim, California, in April 1995. For various reasons we had to postpone it for two years. Meanwhile, my colleague Prof. O. Yavuz Ataman of the Middle East Technical University had organized the first meeting in November 22, 1996 at the Chemistry Department of METU where Prof. H. B. Mark Jr. of University of Cincinnati and several scientists from Turkey discussed several aspects of the recent developments on "Conducting Polymers".

I had attended the first national delegates meeting for COST Action 518 on "Molecular Materials and Functional Polymers for Advanced Devices" in Brussels in February, 1997. As for the second delegates meeting, I made the suggestion to conduct it in Turkey and combine it with the planned workshop with Prof. Zerbi. The idea was welcomed by all the attendants and Dr. Lobotka was able to persuade his higher authorities. The name and the scope of the workshop had to be altered accordingly.

My initial expectations for the workshop was about 5-6 talks by speakers from outside of Turkey and a similar number from our national colleagues. I was pleasantly surprised in ending up with 20 papers. Some of the authors agreed to submit their papers for publication of this special issue of the Turkish Journal of Chemistry. The 12 papers presented in this issue are those papers.

I convey my sincere appreciation to all contributors to the workshop as well as to this special issues. Furthermore, I thank especially to;

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Şefik SÜZER, The Guest Editor