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## Surface modification of a reactive metal or alloy by polyaniline for electrooxidation of iodide

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**Abstract** Generally, an inert metal such as platinum is used for studying electrooxidation reactions. As a non-platinum metal or alloy undergoes corrosion and oxidation, it is not useful for this purpose. In the present study, surface modification of non-platinum metals by coating electronically conducting polymers for electrooxidation reactions was investigated. Polyaniline (PANI) was electrochemically deposited on stainless steel (SS) substrate by potentiodynamic method. The oxidation of  $I^-$  was studied by cyclic voltammetry and amperometry experiments. The  $I^-/I_2$  reaction couple was found to be quasireversible on the PANI/SS electrode. The amperometry study, conducted under fast mass transport conditions, has provided linear relationship between current and concentration of  $I^-$ . The data were analyzed and rate constant of the reaction was evaluated. Thus the oxidation of  $I^-$ , which does not occur on bare SS electrode, was shown to occur through electron transfer mediated by polyaniline.

**Keywords** Corrosion and oxidation · Stainless steel · Polymers · Deposition · Iodide ion

### Introduction

For studying electrooxidation reactions of dissolved species in aqueous media, it is generally considered essential to employ an inert, noble metal such as Pt or Au anode [1]. Non-noble metals or alloys, such as nickel or stainless steel (SS), are not useful for this purpose because they undergo corrosion in aqueous electrolytes. Consequently, the electrodes are dimensionally unstable and their surfaces are covered with oxide and hydroxide

films. Also, the electrolyte gets contaminated with metallic ions from corrosion products. More importantly, the non-noble metal itself undergoes electrooxidation in preference to the oxidation of the reactant present in the electrolyte. As a result, the desired electrooxidation reaction cannot be studied on a non-noble metal or alloy.

Electronically conducting polymers, namely, polyaniline (PANI), polypyrrole, polythiophene, etc. possess interesting electrochemical properties [2, 3]. PANI is synthesized by oxidative polymerization of aniline in chemical as well as electrochemical routes [4]. The electrooxidation of aniline produces a film of PANI on the surface of the anode used. For this purpose also, the electrodes generally employed are made of inert metals such as Pt or Au because the electrolyte is an acidic solution containing dissolved aniline [4]. If the polymerization is carried out on a reactive metal (e.g., nickel, stainless steel, etc.) by a potentiodynamic technique, the metal undergoes oxidation initially. Despite this, the oxidation of aniline takes place at potentials  $> 0.9$  V versus saturated calomel electrode (SCE) and a film of PANI forms on the reactive metal [5]. The PANI covered non-noble metal electrodes show interesting electrochemical properties [6].

Studies on electrooxidation of  $I^-$ , and electrochemical reversibility of  $I^-/I_2$  were of fundamental importance [1]. Also, the diffusion current of  $I_2$  or  $I_3^-$  ion was used in micro-iodometric studies [7]. Several investigations on this electrochemical reaction were reported [8–10]. In all these studies, the electrodes are made of Pt. Oxidation of  $I^-$  on PANI was also reported [11]. However, the substrate used in this study is also Pt. Because the bare Pt surface itself supports the  $I^-/I_2$  reaction, the use of PANI deposited Pt does not attract much interest. On the other hand, the effect of PANI on the reaction kinetics would be more interesting if the substrate used for PANI is a non-platinum metal or alloy, which does not favor the reaction to take place on its bare surface. To the best of the authors' knowledge, the  $I^-/I_2$  reversible reaction has not been studied on either a bare

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or a surface modified non-noble metal or alloy. In the present study, it is shown that PANI covered SS is useful for studying  $I^-/I_2$  redox reaction. A real effect of the conducting polymer towards electrode kinetics is demonstrated.

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## Materials and methods

Analar grade chemicals and doubly distilled water were used for preparation of solutions. Aniline was subjected to vacuum distillation before use. A SS foil of grade 304 was polished, cleaned with a detergent and rinsed with double distilled water. A glass cell of about 100 ml capacity with necessary provisions for introducing the working electrode between two auxiliary Pt electrodes, and a SCE was employed for electrochemical studies. All potential values are reported against SCE. Electrochemical deposition of PANI on a SS foil of area  $0.6 \text{ cm}^2$  was carried out by potential cycling between  $-0.2 \text{ V}$  and  $1.2 \text{ V}$  in an electrolyte of  $0.5 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M aniline}$  at a sweep rate of  $100 \text{ mV s}^{-1}$ . The electrode was cycled repeatedly. The thickness of PANI increases with an increase in the number of potential cycles. Cyclic voltammetry experiments were carried out using a computer-controlled potentiostat/galvanostat EG&G PARC Model Versastat. For amperometry experiments, the electrolyte was kept under continuous stirring, the potential of a PANI/SS electrode was fixed at a required value and steady values of current were recorded at several concentrations of KI. All experiments were carried out at  $20 \pm 1^\circ\text{C}$ .

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## Results and discussion

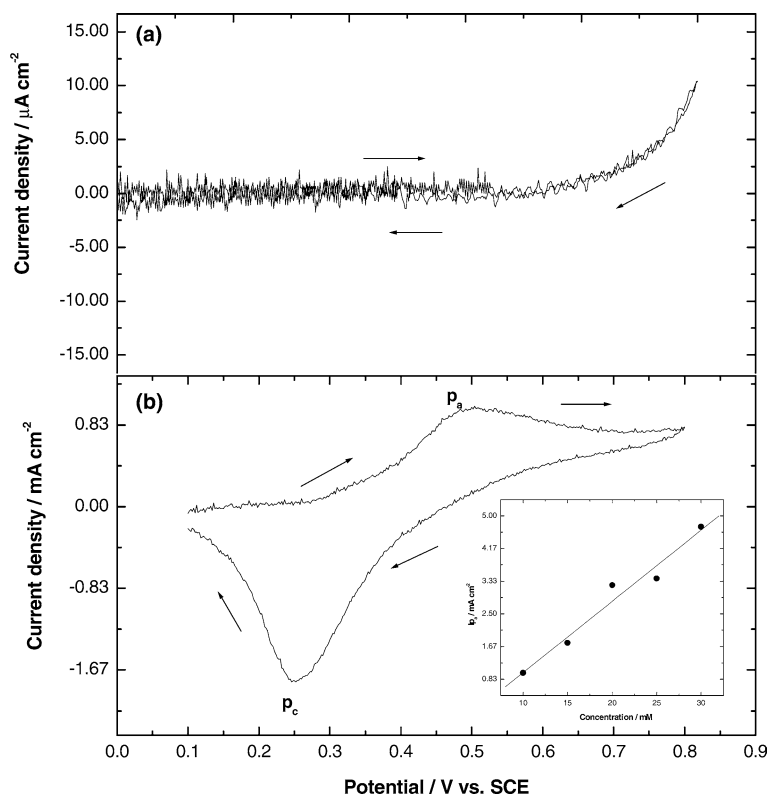
The cyclic voltammograms recorded during the deposition of PANI revealed oxidation of SS substrate at about  $0.2 \text{ V}$  before the oxidation of aniline takes place at about  $1.0 \text{ V}$ . The later process produces a thin layer of PANI on the electrode surface. The charge associated with oxidation of aniline is several times higher than that of the substrate oxidation. The polymer film formed during the initial cycle protects the SS from further oxidation during the subsequent potential cycles [5]. As repeated potential cycles were used for coating of PANI and some amount of PANI deposits on the electrode during each cycle, the voltammetric charge increases with the number of sweeps. The charge of a voltammogram in the potential range between  $-0.2 \text{ V}$  and  $1.2 \text{ V}$  includes the charge corresponding to redox processes of PANI coated up to the previous cycle in addition to the oxidation of aniline. Consequently, the substrate oxidation charge has negligibly small contribution to the voltammetric charge measured for the final voltammogram. The charge of the ending voltammogram is a measure of the thickness of PANI.

For studying the electrooxidation of  $I^-$ , PANI was deposited on SS by sweeping the electrode twice in  $0.5 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M aniline}$  at a rate of  $100 \text{ mV s}^{-1}$ . The charge of anodic part of the voltammogram was  $33 \text{ mC cm}^{-2}$ . A correlation between the voltammetric charge and thickness of PANI was established by Stilwell and Park [12]. Assuming that the same relationship holds good in the present study also, a thickness of  $0.23 \mu\text{m}$  is obtained for the PANI film prepared from two potential cycles. Cyclic voltammogram recorded in  $0.5 \text{ M H}_2\text{SO}_4$  consisting of  $0.01 \text{ M KI}$  using this electrode (hereafter referred to as PANI/SS electrode) is shown in Fig. 1. For comparison, the voltammogram of a bare SS electrode (Fig. 1a) does not show any current peaks. On the other hand, the voltammogram of PANI/SS electrode (Fig. 1b) consists of an oxidation peak ( $p_a$ ) at  $0.50 \text{ V}$  in the forward sweep and a reduction peak ( $p_c$ ) at  $0.25 \text{ V}$  in the reverse sweep. It is found that the current peaks of PANI/SS electrode increase with an increase in concentration of KI in  $0.5 \text{ M H}_2\text{SO}_4$  (Fig. 1b inset). Thus the  $p_a$  is attributed to oxidation of  $I^-$  and the  $p_c$  to a reduction process.

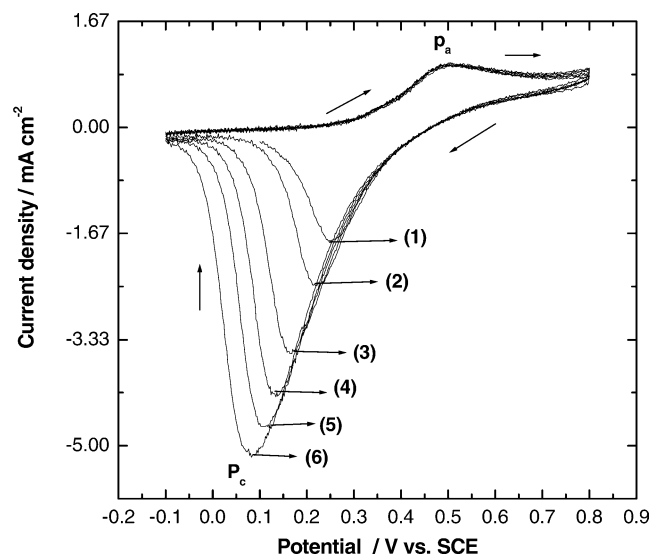
During the forward potential sweep, the oxidation of  $I^-$  to  $I_2$  molecule involves a transfer of two electrons and the reversible potential of this reaction is  $0.387 \text{ V}$ . The  $I_2$  thus evolved forms a thin film at the electrode surface [11]. In the concentrated solution,  $I_2$  can combine with  $I^-$  producing  $I_3^-$ . It is also possible that  $I^-$  can be oxidized directly to  $I_3^-$  in a single step. The oxidations of  $I^-$  to  $I_2$  and  $I_3^-$  are reportedly identified by a pair of anodic current peaks of cyclic voltammograms [11]. During the reverse sweep, reduction of  $I_3^-$  and  $I_2$  occurs to  $I^-$ . A split in the cathodic peaks was attributed to these two steps [11]. In the present work, there is a single anodic peak and a single cathodic peak (Fig. 1a) without splitting. As the peak potential separation of  $p_a$  and  $p_c$  in Fig. 1b is about  $0.25 \text{ V}$ , which is several times higher than  $0.03 \text{ V}$  expected for a reversible two-electron transfer process, the  $I^-/I_2$  reaction couple is considered quasi-reversible on PANI/SS electrode. Furthermore, from the potential of  $p_a$  ( $0.50 \text{ V}$ ) and the potential of  $p_c$  ( $0.25 \text{ V}$ ), the average peak potential becomes  $0.37 \text{ V}$ , which is close to the reversible potential ( $0.387 \text{ V}$ ) of  $I^-/I_2$  couple. Thus, the PANI film on SS substrate facilitates the electron-transfer reaction. The nature of voltammograms recorded for  $I^-/I_2$  couple using PANI deposited on other non-platinum metals, e.g., Ni, are similar to the voltammogram shown in Fig. 1 for PANI/SS electrode. Thus the reactive non-platinum metals, which do not facilitate the  $I^-/I_2$  reaction on their bare surfaces, are modified by the PANI film allowing the reaction to occur.

Cyclic voltammograms were also recorded in  $0.5 \text{ M H}_2\text{SO}_4 + 0.01 \text{ M KI}$  electrolyte using a PANI/SS electrode repeatedly at a sweep rate of  $10 \text{ mV s}^{-1}$ , but by holding the potential for different durations at the switching potential before reversing the sweep direction (Fig. 2). It is seen that the anodic parts of all voltammograms recorded during the forward potential sweep

**Fig. 1** Cyclic voltammograms of **a** bare SS electrode and **b** PANI/SS electrode in 0.5 M  $\text{H}_2\text{SO}_4 + 0.01$  M KI at a sweep rate  $10 \text{ mV s}^{-1}$ . Anodic peak current ( $I_{pa}$ ) versus concentration of KI in 0.5 M  $\text{H}_2\text{SO}_4$  is shown as the inset of **(b)**



merge together thus suggesting an excellent reproducibility of oxidation of  $\text{I}^-$ . The cathodic peak current, however, increases with an increase in the time of holding the electrode at the switching potential. By holding the electrode at a potential positive to the peak, the oxidation of  $\text{I}^-$  continues during the holding period resulting in an increase in concentration of  $\text{I}_2$  at the

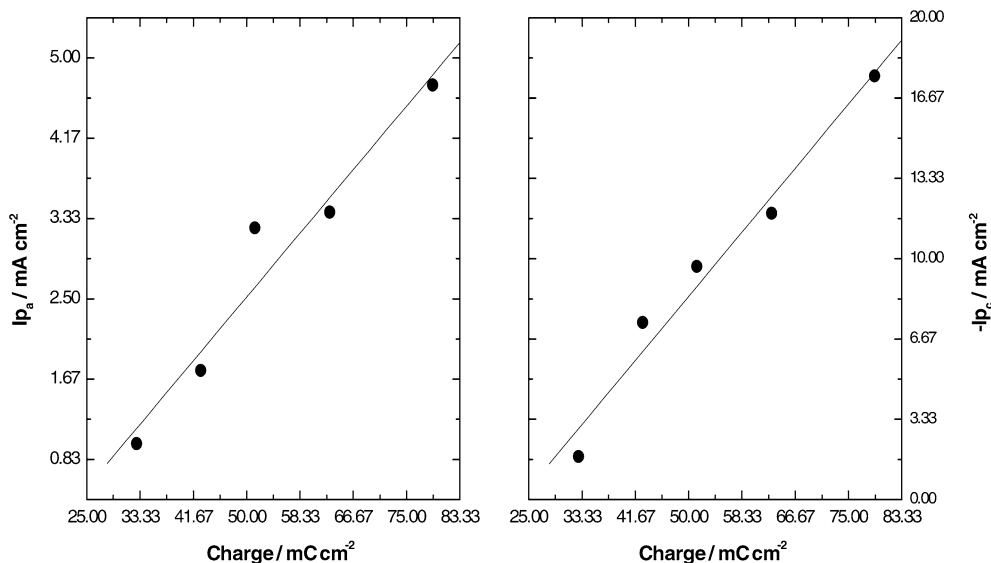


**Fig. 2** Cyclic voltammograms of PANI/SS electrode in 0.5 M  $\text{H}_2\text{SO}_4 + 0.01$  M KI at a sweep rate of  $10 \text{ mV s}^{-1}$  by holding the electrode at 0.80 V versus SCE for (1) 0, (2) 60, (3) 120, (4) 180, (5) 240, and (6) 300 s before reversing the sweep direction

electrode surface. Thus the concentration of  $\text{I}_2$  increases with an increase of holding time. Consequently, the cathodic peak current increases during the reverse direction of the experiments. It is also seen in the Fig. 2 that there is a shift in the cathodic peak potential in the negative direction. This is attributed to ohmic drop with an increase in current. Accumulation of the non-conducting  $\text{I}_2$  at the PANI/SS electrode formed during the forward sweep is responsible for the ohmic drop. In another set of experiments, voltammograms were recorded by varying the switching potentials in the range of 0.6–0.9 V. In these experiments, the sweep was reversed without holding the electrode at the switching potential. In these experiments also, while the anodic peak current remained reproducible, the cathodic peak current increased with an increase in switching potential. This is due to the fact that the residence time of the electrode in the anodic direction increases during the forward sweep thus producing increased concentration of  $\text{I}_2$ . Consequently, there is an increase in the cathodic peak current due to an increase in the switching potential.

On the PANI/SS electrode immersed in an electrolyte solution, three different interfaces exist [11]: (1) the interface between SS and PANI, (2) the internal PANI/solution interface inside the porous PANI film, and (3) the external PANI/solution interface on the external surface of the PANI film. Thus for the reaction to take place one possibility is that the  $\text{I}^-$  ion diffuses from the bulk of the solution to the external surface of the PANI and undergoes oxidation. Diffusion of  $\text{I}^-$  ion inside the

**Fig. 3** The effect of thickness of PANI on **a** the anodic peak current ( $I_{pa}$ ) and **b** cathodic peak current ( $I_{pc}$ ) of cyclic voltammograms of PANI/SS electrodes in 0.5 M  $H_2SO_4 + 0.01$  M KI at a sweep rate of  $10 \text{ mV s}^{-1}$ . Thickness of PANI is expressed as the charge of its deposition by potentiodynamic method

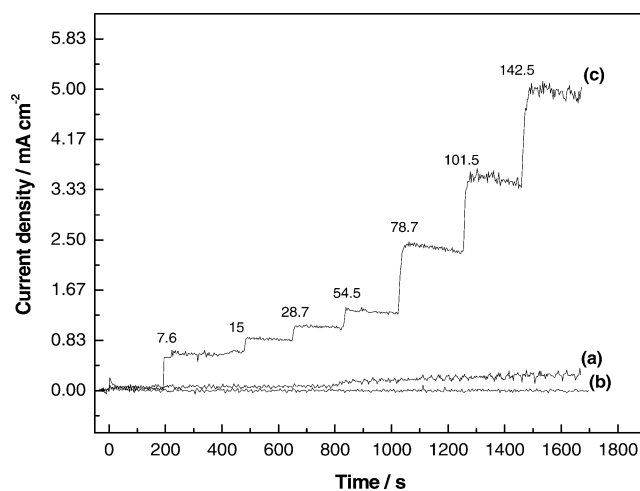


porous PANI film, and further to the surface of SS uncovered by the polymer before undergoing oxidation at these regions are the other possibilities. It is shown in Fig. 1a that the bare SS surface does not allow the oxidation of  $I^-$ , and therefore the interface between SS and PANI is not considered important. Thus the internal PANI/solution interface is a possible region in addition to the external PANI/solution interface for the oxidation. The area of the internal PANI/solution interface increases with an increase in thickness of PANI. To examine the contribution of internal PANI/solution interface, cyclic voltammetric experiments were performed with PANI of different thicknesses. The SS electrodes were subjected to the required number of repeated potential sweeps in 0.5 M  $H_2SO_4 + 0.1$  M aniline for increasing the thickness of PANI. Using these electrodes, cyclic voltammograms were recorded in 0.5 M  $H_2SO_4 + 0.01$  M KI. It is seen that there is an increase in currents of both anodic and cathodic peaks with an increase in PANI thickness, as shown in Fig. 3. It is thus concluded that the internal PANI/solution interfacial region contributes significantly for the reversible  $I^-/I_2$  reaction to take place.

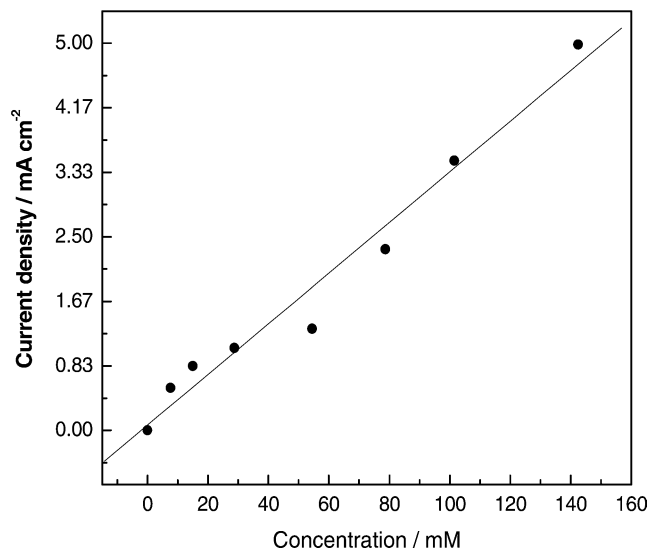
Subsequent to confirmation that the  $I^-/I_2$  reversible process takes place on PANI/SS electrode, further experiments were conducted by using amperometry for calculation of the rate constant of oxidation of  $I^-$ . The potential of a PANI/SS electrode was held at 0.80 V in a stirred electrolyte of 0.5 M  $H_2SO_4$ , and steady values of current were measured when known amounts of KI were added to the electrolyte. A variation of current flowing through a PANI/SS electrode due to changes in concentration of KI is shown in Fig. 4. Also shown in Fig. 4 are the current response of bare SS to the changes in concentration of KI and that of a PANI/SS electrode in supporting electrolyte alone (i.e., in the absence of KI). It is seen that the bare SS electrode does not respond to the concentration changes, thus supporting the cyclic

voltammetric data (Fig. 1a). On the other hand, there is an increase in current of PANI/SS electrode with increase in concentration of KI. At each stage of change in concentration, the current value was found constant for about 5 min measured. The constancy of current suggests that the mass transfer is fast due to stirring of the electrolyte and therefore the oxidation of  $I^-$  is under charge-transfer control. Furthermore, the current flowing through the PANI/SS electrode in the absence of KI is negligibly smaller than the oxidation currents (Fig. 4). A plot of current versus concentration is linear as shown in Fig. 5 for the experiment at 0.80 V. The relationship between current density ( $I$ ) and concentration ( $c$ ) is given as

$$I = nFkc \quad (1)$$



**Fig. 4** Steady-state oxidation current flowing at 0.80 V versus SCE through a bare SS electrode (a) and PANI/SS electrodes (b and c) in 0.5 M  $H_2SO_4$ . Curves a and c were recorded by increasing the concentration of KI as indicated in mM, and b in the absence of KI



**Fig. 5** Variation of current density of a PANI/SS electrode with concentration of KI in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 0.80 V versus SCE

where  $n$  is the number of electrons ( $=2$ ),  $F$  is the Faraday constant and  $k$  is the rate constant of the reaction, which is a potential-dependent parameter. Equation (1) is valid for reactions with fast mass transfer step and therefore the electron-transfer step is rate-determining. In the present experiment, fast mass transfer was ensured by a uniform stirring of the electrolyte using a magnetic bar. On differentiation of Eq. (1), we get

$$(dI/dc) = nFk \quad (2)$$

Thus from slope of the plot in Fig. 5, the value of  $k$  is calculated as  $1.67 \times 10^{-4} \text{ cm s}^{-1}$  at 0.80 V.

## Conclusions

For the study of oxidation of  $I^-$  in acidic electrolytes, generally an inert electrode such as Pt is required. The reaction does not take place on a non-platinum metal such as SS. In the present study, it is shown that the  $I^-/I_2$  reaction takes place on PANI-covered SS electrodes. The nature of the reaction is quasireversible, as found from the cyclic voltammetric studies. The rate constant of the reaction is estimated from charge-transfer controlled amperometric studies.

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