

Enhancement of electron transfer kinetics on a polyaniline-modified electrode in the presence of anionic dopants

S. Ghasemi · M. F. Mousavi · M. Shamsipur

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Abstract The electrocatalytic redox behavior of 1,4-naphthoquinone (NQ) has been studied on a polyaniline-modified platinum electrode (PANI) using cyclic voltammetry and rotating disc electrode (RDE) as diagnostic techniques. The modified electrode was prepared by electropolymerization of aniline in different acidic solutions. The PANI showed electrocatalytic activity toward the redox behavior of NQ. This process includes the participation of PANI to the redox reaction of NQ via the surface catalysis phenomena. The cyclic voltammograms of NQ in HCl on the PANI-Cl-modified electrode showed an overlapped oxidation peak, the peak potential of which did not change with increasing scan rate. The influence of other anions including ClO_4^- and SO_4^{2-} as dopant was also studied and compared with Cl^- . The use of $HClO_4$ as a supporting electrolyte resulted in well-separated redox peaks. The RDE voltammogram was used to obtain a quantitative assessment of reaction rate at the PANI-modified electrode. It was found that PANI acts as an electrocatalyst for NQ reduction with decreasing ΔE_p and increasing k^0 .

Keywords Polyaniline-modified electrode · 1,4-Naphthoquinone · Anion effect · Electrocatalysis

Introduction

A promising approach for minimizing overvoltage effects in electrocatalytic processes is the use of chemically modified

electrodes [1–6]. A thin layer of a modifier, deposited on the surface of the electrode, is able to enhance the kinetics of electrode process of some solution species which give rise to an attractive area of investigation in various fields of electrochemistry such as gas sensors [7], biosensors [8, 9], corrosion control [10], and batteries [11–13]. Among different materials used for the modification of electrode surfaces, the conducting polymers have been shown to be of critical interest [14–16]. Polyaniline (PANI) as an intrinsically conducting polymer can catalyze some electrode processes with heterogeneous electron transfer between the electrode and polymer [17–22]. Quinone–hydroquinone redox couples [23, 24], organic compounds of analytical interest such as ascorbic acid [25], reduced form of nicotinamide adenine dinucleotide phosphate [NADPH (H)] [26], H_2O_2 [27], N_2H_4 [28] on PANI and reduction in O_2 [29], electrooxidation of methanol on PANI with dispersed metals [30], glucose [31, 32], nitrite [33], urea [34], choline [35], and glycerol [36] are examples of compounds that have been studied for their electrocatalytic behaviors.

Numerous quinones play vital roles in the bioelectrochemistry of living cells and exert relevant biological and physiological activities in animals and plants [37–39]. 1,4-Naphthoquinone (NQ) composes a backbone for many compounds such as phthiocol, various pigments, vitamin K, and many antitumor drugs which are involved in biological activities [40, 41]. A series of investigations have been carried out on the electrochemical characterization of substituted NQs.

Lebedev et al. [42] observed the surprising effect of Ca^{2+} on the redox reaction of Echinochrome A (6-ethyl-2,3,5,7,8-pentahydroxyquinone), as a pigment of sea urchins. Ferraz et al. [43] investigated the electrochemical aspects of the reduction of the biological active 2-hydroxy-3-alkyl-1,4-naphthoquinone. Oyama et al. [44] have revealed that, in general, it is thermodynamically possible for species to be

S. Ghasemi · M. F. Mousavi (✉)
Department of Chemistry, Tarbiat Modares University,
P. O. Box: 14115-175, Tehran, Iran
e-mail: mousavim@modares.ac.ir

M. Shamsipur
Department of Chemistry, Razi University,
Kermanshah, Iran

oxidized or reduced by PANI if the redox potential of a redox couple is within the potential window, in which PANI film is electroactive. Morphology of polymer, induced with counterions [23], location of reaction [45], and thickness effect [23, 45] are of interest in the research field in the electrocatalytic study of PANI film. Malinauskas et al. [45] investigated the cathodic reduction of 1,2-naphthoquinone-4-sulfonate (NQS) at PANI-coated ITO glass electrode with UV-visible spectroelectrochemistry. An electrocatalytic behavior was observed which includes the cathodic reduction of the PANI film and its subsequent reoxidation by NQS. In this case, PANI acts as a redox mediator cycled between its emeraldine (EM) and leucoemeraldine (LE) forms.

In this work, we investigated PANI-modified electrodes (PANI), prepared from different acid solutions, i.e., hydrochloric, perchloric, and sulfuric acid, doped with different dopants, and found out that these electrodes have a pronounced electrocatalytic effect on the NQ/H₂NQ reaction. The novelty of the present work lies in the fact that the electrocatalytic activity of the modified electrodes prepared in the presence of anionic dopants, especially ClO₄⁻, shows a significant improvement over most of the previous proposed electrodes [23, 46].

Materials and methods

Materials

Aniline (Aldrich) was distilled before use and kept in dark-cool situations. NQ and all other reagents were of analytical grade from Merck and used without further purification. Doubly distilled water was used throughout.

Instrumentation

A Metrohm multipurpose instrument model 746 VA Trace Analyzer with a 747 VA stand was used to perform the electrochemical experiments. A conventional one-compartment, three-electrode cell equipped with a platinum disk electrode (2 mm diameter) as the working electrode, a platinum wire as auxiliary electrode, and an Ag/AgCl, KCl (3 M) as reference electrode. All potentials in the text are quoted vs this reference electrode. In addition, all studies were carried out in an argon atmosphere and at room temperature.

Procedures

The platinum disk electrode was further polished with 0.04 μm α-alumina powder on a polishing micro-cloth and rinsed thoroughly with doubly distilled water before each experiment. The solutions were deaerated with argon

(99.999%, Rohamgas, Iran), and an argon atmosphere was achieved over the solution in the electrochemical cell.

PANI was deposited on Pt electrodes from 1 M solutions of hydrochloric, sulfuric, or perchloric acid containing 0.1 M aniline by means of consecutive cyclic potentials in the range of 100 to 850 mV and a potential sweep rate of 50 mV s⁻¹. Then, the modified electrodes were rinsed thoroughly with doubly distilled water. Because of the electrochemical degradation of PANI at 850 mV, all voltammograms were taken in the potential range of -100 to 800 mV. The PANI thickness was estimated (Table 1) from the amount of charge Q necessary to switch from the LE to EM form of PANI according to Eq. 1:

$$d = \frac{QM}{zFA\rho} \quad (1)$$

Where M is molecular weight of aniline, A area of electrode (0.0314 cm²), F Faraday's constant; ρ density of aniline (1.02 g cm⁻³), and $z=0.5$ is number of charge of aniline unit in polymer chains [23]. The PANI layer thickness was so thick that the Pt substrate was not expected to have any role in observed behavior. Rotating disc electrode (RDE) voltammograms were recorded for rotation speeds, from 600 to 3,000 rpm, at 4 mV s⁻¹.

Results and discussion

Cyclic voltammetry

Figure 1a compares the cyclic voltammograms of NQ obtained on bare Pt (curve A) and PANI-Cl electrodes (curve B) in 1 M HCl in the range of -0.1 to 0.8 V at a potential sweep rate of 60 mV s⁻¹. The peak potential separation between the anodic and corresponding cathodic peak for the redox behavior of NQ at the bare Pt and the PANI-modified electrode in different supporting electrolytes at a sweep rate 60 mV s⁻¹ was reported in Table 2. In the case of bare Pt

Table 1 Charge and calculated thickness of PANI films

PANI electrode	Charge $Q/\mu\text{C}$	Thickness $d/\mu\text{m}$
PANI-Cl 1	21.74	1.30±0.03
PANI-Cl 2	42.07	2.53±0.05
PANI-Cl 3	67.24	3.97±0.06
PANI-SO ₄ 1	21.31	3.04±0.06
PANI-SO ₄ 2	31.58	1.90±0.03
PANI-SO ₄ 3	50.56	3.04±0.06
PANI-ClO ₄ 1	25.96	1.56±0.03
PANI-ClO ₄ 2	34.43	2.07±0.04
PANI-ClO ₄ 3	56.20	3.38±0.05

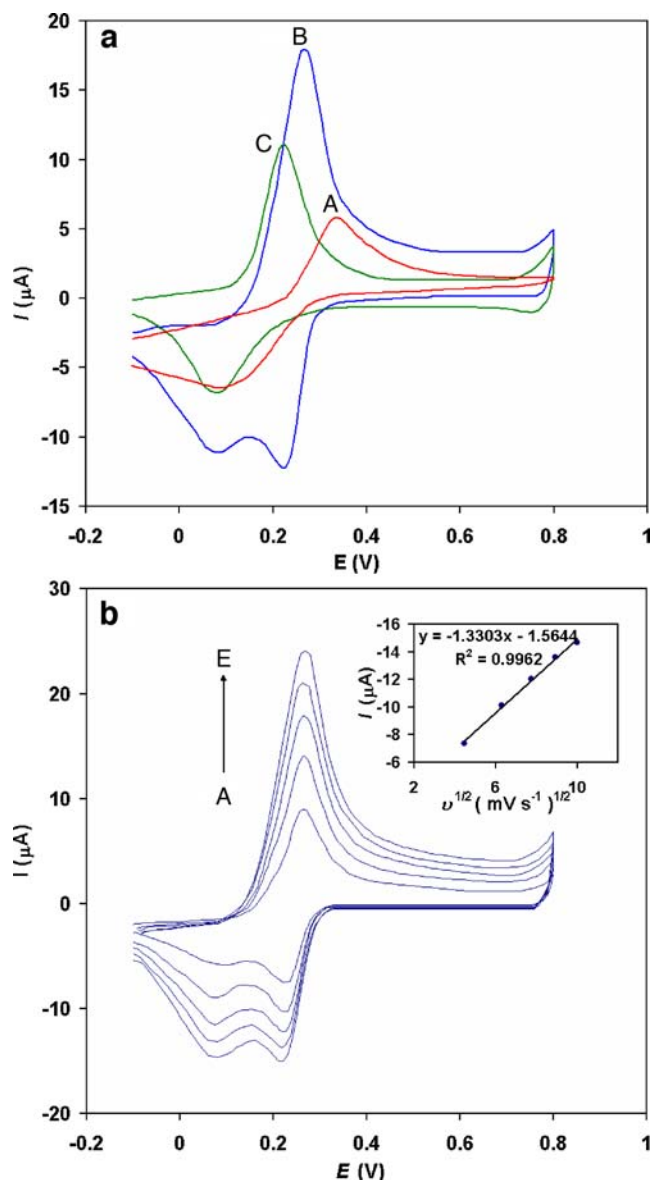


Fig. 1 **a** A comparison between cyclic voltammograms of redox reaction of 5.6×10^{-4} M NQ in 1 M HCl at Pt (A) and PANI-Cl (B) and PANI-Cl in the absence of NQ (i.e., first redox peak of PANI itself; C) at 60 mV s^{-1} . **b** Typical cyclic voltammograms of PANI-Cl-modified electrode in 1 M HCl in the presence of 5.6×10^{-4} M of NQ at different scan rates: (A) 20, (B) 40, (C) 60, (D) 80, (E) 100 mV s^{-1} (inset shows the dependence of cathodic current to square root of potential sweep rate)

electrode, a couple of reduction and oxidation peaks were observed with peak separation of 248 mV at 60 mV s^{-1} (Table 2). The peak separation was increased with scan rate increments. These peaks were attributed to redox reaction of NQ/H₂NQ.

The redox potential of the redox couple is within the potential range of conducting state of PANI, i.e., between LE/EM and EM/pernigraniline (PE) transformation. As it is seen from cyclic voltammogram of PANI-Cl (Fig. 1b) in the presence of 5.6×10^{-4} M NQ and in 1 M HCl, two reduction

peaks were observed while only one oxidation peak appeared at about $E_p = 275 \text{ mV}$. In fact, the anodic peak current of H₂NQ at the PANI-Cl-modified electrode is the sum of the two oxidation peaks for PANI-Cl and NQ, which are strongly overlapped. The potentials of peak do not shift with the increase in the scan rate from 20 to 100 mV s^{-1} (Fig. 1b). The plot of cathodic peak current of NQ (around 225 mV), I_{pc} , against the $\nu^{1/2}$ (inset of Fig. 1b) shows a linear relationship in the range of 20 to 100 mV s^{-1} , indicating that the reaction is diffusion controlled. As seen in Fig. 1a, in comparison with the bare Pt electrode in the case of the PANI-Cl-modified electrode, not only the peak separation for the redox reaction of NQ/H₂NQ couple is significantly decreased but also the corresponding peak currents show a sharp enhancement. The positive sites of PANI in oxidation form (EM) can contribute to electron exchange of NQ with Pt surface. Electron can transfer from NQ/H₂NQ through the PANI chains to the Pt electrode more rapidly, in comparison with the case when the electrode was not modified with PANI.

To identify the observed reduction peaks, the concentrations of NQ in solution were varied from 2.0×10^{-4} M to 5.6×10^{-4} M and the corresponding CV-grams recorded at a scan rate of 60 mV s^{-1} (Fig. 2a). As it is seen, with increasing NQ concentration, the cathodic peak located at 215 mV is increased, while that located at about 70 mV remained unchanged with respect to the corresponding baselines, indicating that the former peak is related to NQ and the later one is related to PANI-Cl.

To get more information about the oxidation peak of H₂NQ from the overlapped oxidation peak, the current values of PANI voltammogram was subtracted from that of H₂NQ on the PANI-Cl-modified electrode. Figure 2b compares the cyclic voltammograms of NQ on bare Pt and on PANI-modified Pt electrodes. Basically, a catalytic system can be easily identified through the decrease in overpotential in addition to current enhancement. From the results obtained, it is evident that PANI acts as an electrocatalyst for NQ/H₂NQ system. The EM form of PANI has a high electrical conductivity (approximately 10^2 S cm^{-1} [36]), but its LE form, at lower potentials than EM, possesses a low conductivity. When the redox potential of redox couples is within the conductive state of PANI (EM), the reaction of reactants accelerates at the polymer/solution interface. On the other hand, when the

Table 2 ΔE_p values for the redox behavior of NQ on bare Pt and PANIs in different supporting electrolytes at 60 mV s^{-1}

Substrate	Pt			PANIs		
Anionic dopant	Cl ⁻	SO ₄ ²⁻	ClO ₄ ⁻	Cl ⁻	SO ₄ ²⁻	ClO ₄ ⁻
ΔE_p	248±4	205±2	212±4	42±3	31±2	42±3

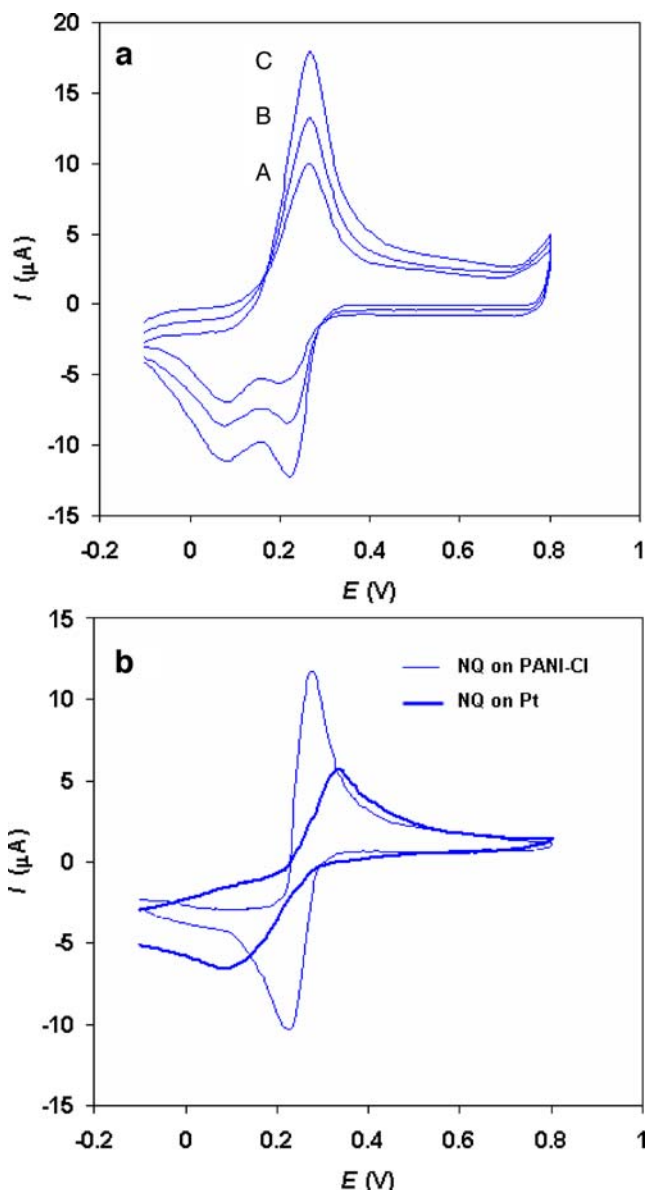


Fig. 2 **a** Cyclic voltammograms of different concentrations of NQ on PANI in 1 M HCl at 60 mV s^{-1} . NQ concentrations are: (A) $2.0 \times 10^{-4} \text{ M}$, (B) $4.0 \times 10^{-4} \text{ M}$, (C) $5.6 \times 10^{-4} \text{ M}$; **b** comparison of cyclic voltammograms $5.6 \times 10^{-4} \text{ M}$ of NQ in 1 M HCl at 60 mV s^{-1} after subtracting current of PANI-Cl from current of NQ on PANI-Cl modified electrode

redox potential of reactant is in LE state, no redox process of solution species can be achieved at PANI film. However, because of porous structure of PANI, the small electroactive species can diffuse through the film to the electrode surface and electrode redox process can occur at the substrate electrode/electrolyte interface [36].

Effect of dopants

To overcome the overlapping problem and separate the two oxidation peaks related to PANI and NQ, the effect of other

doping anions such as SO_4^{2-} and ClO_4^- were examined. Figure 3 shows the cyclic voltammograms of PANI- SO_4 in the presence of $5.6 \times 10^{-4} \text{ M}$ NQ in 1 M H_2SO_4 . As seen in Fig. 3, a peak separation was observed when scan rate was 20 mV s^{-1} and lower, while at higher scan rates, no peak separation was observed (Fig. 3).

The behavior of PANI- ClO_4 -modified electrode was investigated in the presence of $5.6 \times 10^{-4} \text{ M}$ NQ in 1 M HClO_4 solution at various sweep rates from 20 to 100 mV s^{-1} , and the results are depicted in Fig. 4a. The cyclic voltammograms show two nice distinct oxidation peaks, one of which is related to NQ and the other to the first oxidation stage of PANI- ClO_4 (Fig. 4a). Moreover, an increase in the NQ concentration from 2.0 to $5.6 \times 10^{-4} \text{ M}$, resulted in an enhancement of the cathodic peak at about 205 mV and the anodic peak at about 265 mV, whereas the other pair of peaks remained unchanged. Thus, the 205/265 mV pair should be related to the redox reaction of NQ.

When the current of NQ on PANI- ClO_4 was subtracted from that of PANI- ClO_4 alone, the cyclic voltammogram of NQ on PANI- ClO_4 was obtained (Fig. 4b), which is similar to NQ on PANI-Cl. The plots of cathodic peak current of NQ against square root of scan rate on PANI- SO_4 -modified electrode in 1 M H_2SO_4 (inset of Fig. 3) and PANI- ClO_4 -modified electrode in 1 M HClO_4 (Fig. 4c) show a linear relation which indicates that the reduction of NQ on PANI- SO_4 and PANI- ClO_4 -modified electrodes is diffusion controlled.

The plots of both oxidation and reduction peak currents of H_2NQ against square root of scan rate on PANI- ClO_4 modified electrode in 1 M HClO_4 shows a linear relationship (Fig. 4c) in the range of 20 to 100 mV s^{-1} , indicating that the reaction is diffusion controlled.

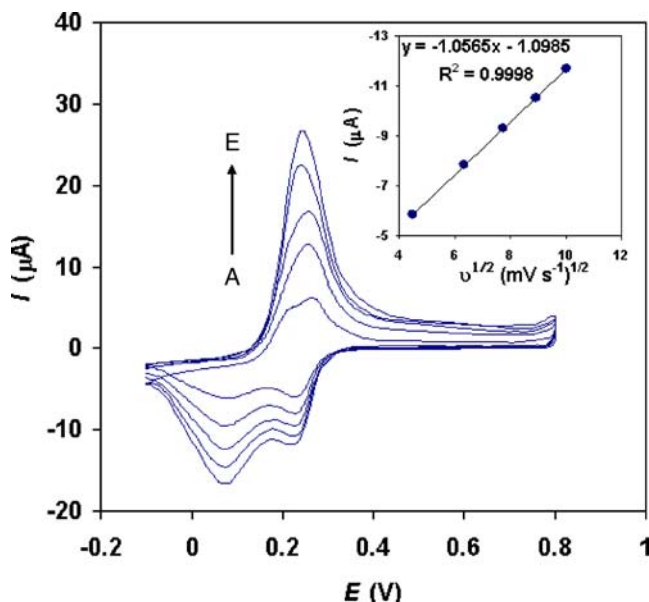


Fig. 3 Cyclic voltammograms of $5.6 \times 10^{-4} \text{ M}$ NQ in 1 M H_2SO_4 on a PANI- SO_4 -modified electrode at different scan rates: (A) 20, (B) 40, (C) 60, (D) 80, (E) 100 mV s^{-1}

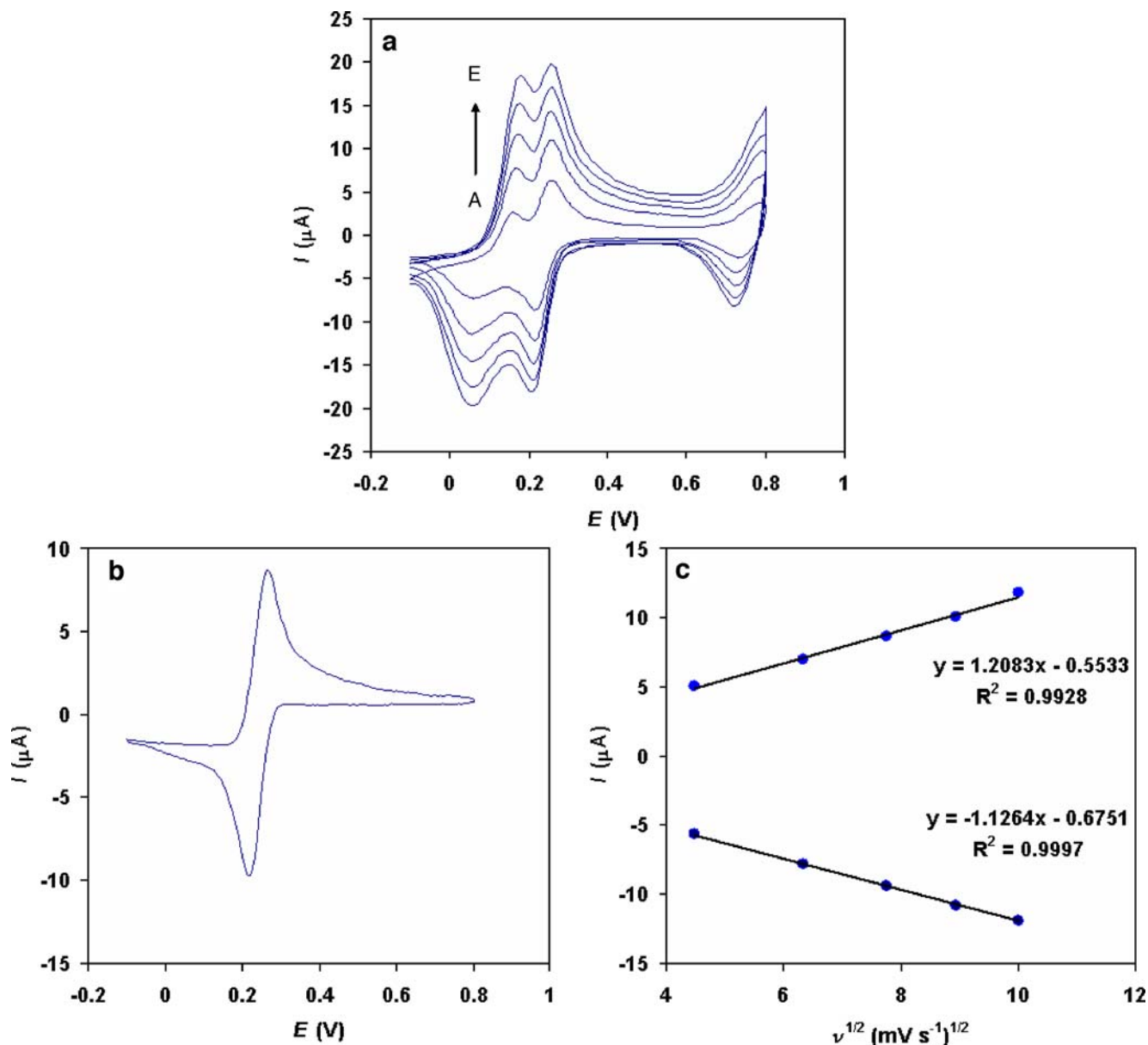


Fig. 4 a Cyclic voltammograms of 5.6 × 10⁻⁴ M NQ at PANI-ClO₄-modified electrode from 0.1 M aniline+HClO₄, in 1 M HClO₄, at different scan rates: (A) 20, (B) 40, (C) 60, (D) 80, (E) 100 mV s⁻¹. b Cyclic voltammogram of 5.6 × 10⁻⁴ M NQ in 1 M HCl on PANI-

ClO₄-modified electrode at a scan rate of 60 mV s⁻¹, after subtracting current of PANI-ClO₄ from current of NQ. c Plot of *I*_p vs *ν*^{1/2} for oxidation and reduction peak of NQ/H₂NQ

In Table 2 are shown the values of Δ*E*_p for NQ/H₂NQ redox process at a bare Pt and PANIs in the presence of different dopant anions. As can be seen from Table 2, the Δ*E*_p values for NQ/H₂NQ redox process are significantly decreased on all three PANIs, in comparison with those on a bare Pt electrode which, in conjunction with the observed current enhancements, are evidences for the occurrence of an electrocatalytic process.

Figure 5 compares the cyclic voltammograms of the PANI films synthesized in different acidic solutions. As is obvious, the peak potentials of LE/EM have different values for the

three different PANI films. These differences in peak position can be explained by the differences in potential distribution which appear in the corresponding conducting polymer/electrolyte interfaces. The potential distribution is determined by permeability of the ions into the polymer layer. It is well known that PANI-ClO₄ has an open structure, but PANI-Cl and PANI-SO₄ possess a closed one, which determine the morphology of polymer [23]. Because the PANI layer possesses ion-exchange properties, determined by the presence of positively charged nitrogen atoms in the polymer chain, a Donnan potential (Δφ) exists across the

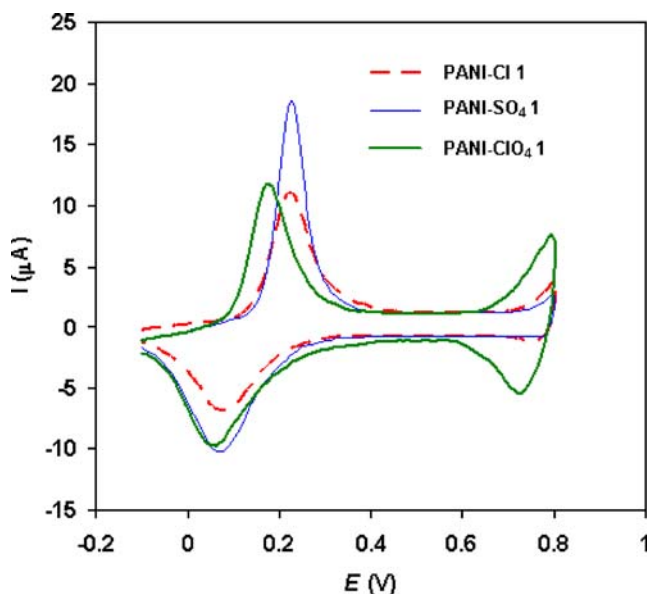


Fig. 5 Comparison of cyclic voltammograms of the first redox peak of PANI-Cl, PANI-SO₄, PANI-ClO₄ at 60 mV s⁻¹

polymer/solution interface. If the reactant has an electric charge of same sign as Donnan potential, an electrostatic repulsion between reactant and polymer membrane occurs. However, when the reactant has no or opposite charge, the redox process can occur effectively on the PANI electrode.

Zhong et al. [47] have reported a membrane-like behavior for the electrolyte/conducting polymer interface so that the potential distribution across interface could be related to the potential distribution at a membrane, and therefore, the potential can be considered as Donnan potential ($\Delta\phi$). In general, the Donnan potential is expressed by the equilibri-

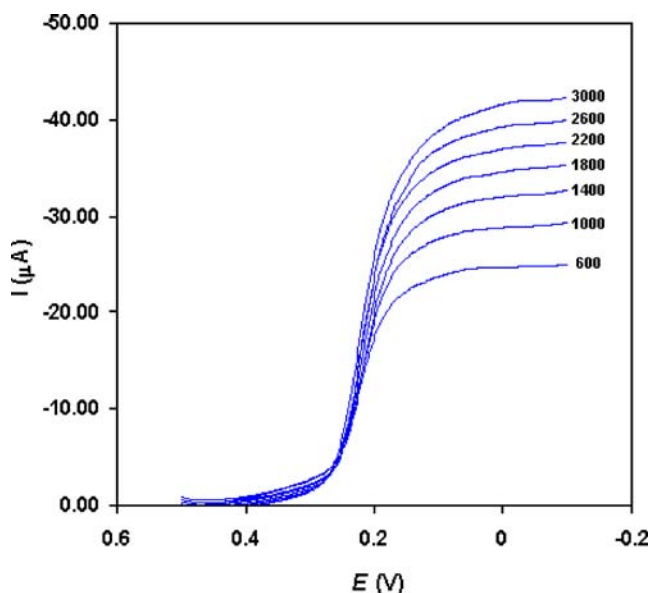


Fig. 6 RDE voltammograms of reduction of 5.6×10^{-4} M NQ at 1 M HClO₄ on PANI-ClO₄ at a scan rate of 4 mV s⁻¹ and $\omega = 600, 1,000, 1,400, 1,800, 2,200, 2,600,$ and 3,000 rpm

Fig. 7 Comparison of RDE voltammograms of reduction of 5.6×10^{-4} M NQ on PANI-ClO₄ (a), PANI-SO₄ (b), and PANI-Cl-modified electrodes in 1 M HClO₄, H₂SO₄ and HCl, respectively (c), at $\nu = 4$ mV s⁻¹ and $\omega = 1800$ rpm at different thicknesses with those on a bare Pt electrode. a', b' and c' Corresponding Koutecky-Levich plots at $\omega = 400, 600, 1,000, 1,400, 1,800, 2,200, 2,600,$ and 3,000 rpm

um concentration of ions at the polymer solution interface (Eq. 2) [46]:

$$\Delta\phi_D = \pm \frac{RT}{F} \operatorname{arcsinh} h \frac{[A_P]}{2[A_S]} \quad (2)$$

Where A_s is the concentration of ions in solution, and A_p is the concentration of charge on the polymer as a scale of ion concentration in polymer. The Donnan potential influences both the permeability of molecules and ions into polymer layer and the charge transfer kinetics. The Donnan potential is related to the redox potential of the system according to Eq. 3:

$$E = E^\circ + \frac{RT}{F} \ln \frac{[EH_2^{2+}]}{[LE]} \pm (\Delta\phi_D) \quad (3)$$

At the current peak potential, the concentration of the [EM] to [LE] ratio can be assumed to be the same for our system; thus, with the change in $\Delta\phi$, the E_p will also be changed. Different values of $\Delta\phi$ cause the different E_p values for LE/EM and EM/PE systems for the three types of PANI films used (Fig. 5) so that different influences can be observed depending on the nature of counterion doped to polymer.

Several papers investigated the mechanism of redox couple on conductive polymers [23, 48–51], most of which proposed the following redox polymer mechanism for the redox process [23]:



The details of the proposed mechanism are discussed by Andrieux et al. [2, 52–55] and Duic and Grigić [23]. In the literature, it has been clarified that the total electrochemical reaction takes place in at least four steps, as follows: (1) diffusion of a reactant to the outer electrode, (2) diffusion of reactant through the layer, (3) charge transfer at the polymer/solution interface within the polymer film, and (4) transport (diffusion) of charge through the polymer to electrode [47, 56].

In this paper, the PANI film acts as a mediator in the charge transfer between the electrode and the dissolved reactant. According to a redox polymer mechanism, for oxidation reaction to proceed at a significant rate, the potential of redox polymer E_{pol} should be higher than or equal to that of the redox reaction of species from the solution [46, 57], whereas

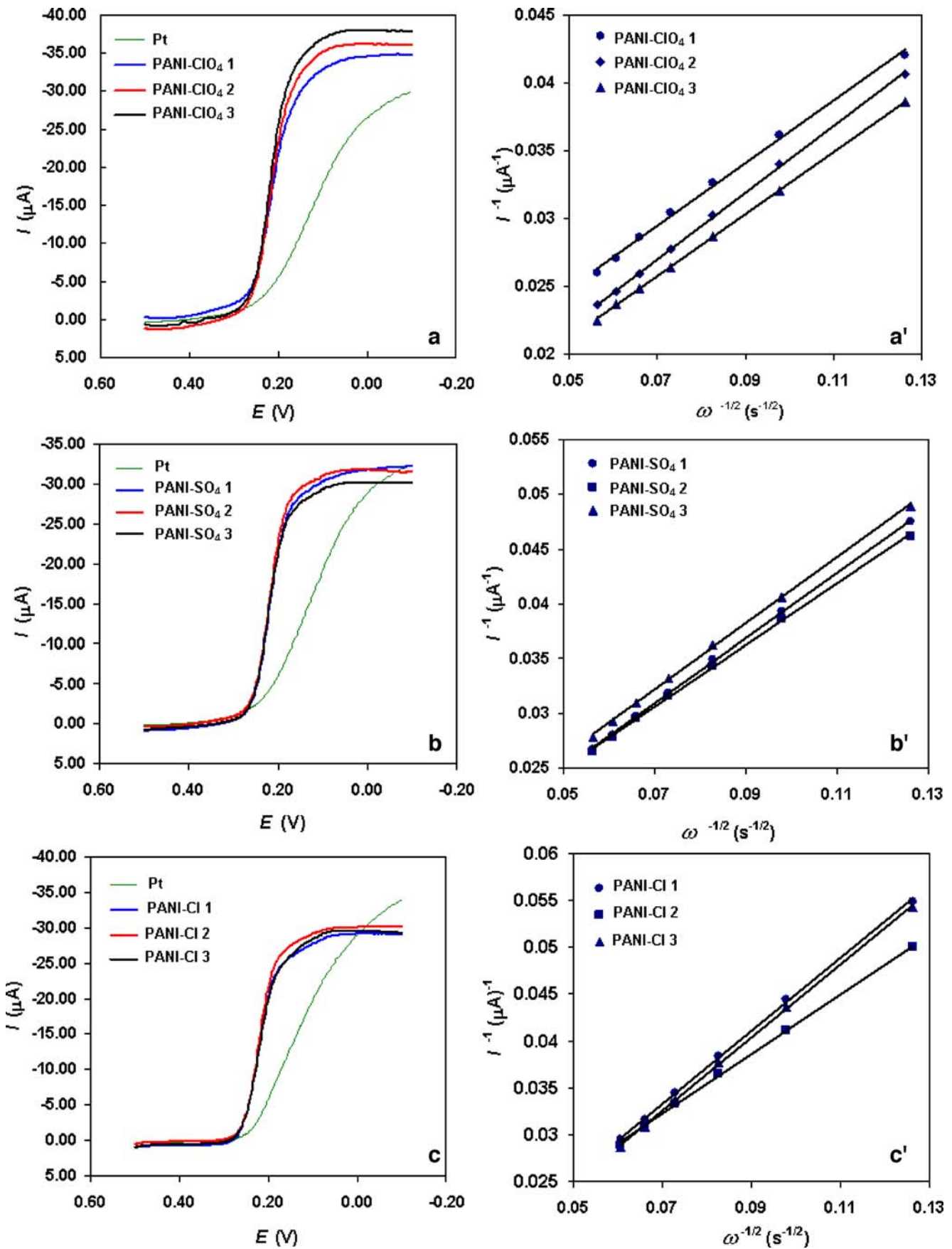


Table 3 The value of k_{ch} at different PANIs

PANI	k_{ch} ($\text{cm}^3 \text{s}^{-1} \text{mol}^{-1}$)
PANI-Cl 1	$1.37 (\pm 0.03) \times 10^7$
PANI-SO ₄ 1	$8.158 (\pm 0.07) \times 10^7$
PANI-ClO ₄ 1	$5.134 (\pm 0.05) \times 10^6$

the potential of LE/EM switching is lower than that of the NQ/H₂NQ reaction.

Levi and Pisarevskaya [58] described phenomenological models of electrochemical reaction at conducting polymer film electrodes. The region of potentials at which the degree of doping is maximal and constant is characterized by a high (quasi-metallic) concentration of the free charge carriers inside which the kinetics are similar to those at the metal electrode. In the case of PANI, in the EM state, the level of doping is maximal and constant. Therefore, PANI in the protonated EM form (EH_2^{2+}) shows the behavior of metal electrode and not of a redox polymer. As a result, depending on the operating potential, PANI acts as a metal substrate (protonated form of PANI) or as a redox polymer (PE form of PANI). Malinauskas and Holze [59] proved the existence of LE form at the EM potential region by in situ spectroelectrochemical measurement of H₂NQ oxidation on PANI electrode. It was shown that the conversion of LE to EM is achieved at different rates so that reoxidation of LE into EM is the rate-determining step in NQ/H₂NQ process.

With increasing the concentration of NQ, the most available EM sites were occupied with the solute. In fact, the electrocatalytic effect will be terminated when all the available EM reaction centers are occupied by the NQ. Meanwhile, the electrocatalytic behavior of polymer is determined by the rate of conversion of LE to EM form, and consequently, the oxidation process should occur at higher potentials.

Hydrodynamic voltammetry

For a more quantitative assessment of the catalysis, the reduction of NQ was examined at a rotating PANI-modified electrode doped with various dopants. Figure 6 shows the RDE voltammograms for reduction of NQ (5.6×10^{-4} M) in 1 M HClO₄ on PANI-ClO₄-modified RDE at various rotation speeds from 400 to 3,000 rpm and at scan rate of 4 mV s^{-1} . The I - E curves possess an “s” shape at various rotation speeds. A comparison between the RDE voltammograms of NQ reduction at the three PANI-modified electrodes, electrosynthesized with different thickness, and that of the bare Pt electrode has been made in Fig. 7a–c. A decrease in NQ reduction potential and an increase in the current-potential slope in RDE measurements are observed for the PANI-modified electrodes with respect to the bare Pt

electrode. These evidences as well as the observed decrease in ΔE_p emphasize the acceleration of reaction and electrocatalytic effect of the PANIs.

The relationship between limiting current I_L and rotation speed ω is given by the Koutecky-Levich Eq. 6 and used for kinetic analysis:

$$\frac{-1}{I_L} = \frac{1}{nFACk_{\text{ch}}\Gamma} + \frac{1}{0.62nFAD^{2/3}\nu^{-1/6}C\omega^{1/2}} \quad (6)$$

Where C is bulk concentration of NQ (mM), Γ is the surface coverage (mol cm^{-2}), k_{ch} is the catalytic rate constant ($\text{cm}^3 \text{s}^{-1} \text{mol}^{-1}$), and all other parameters have their usual meanings. The linear plot of I_L^{-1} vs $\omega^{-1/2}$ with a nonzero intercept indicates a kinetic slow step attributed to the reduction process at all systems (Fig. 7a', b', and c'). It should be noted that the value of rate constant for the catalytic reaction can be obtained from the intercept of the Koutecky-Levich plot (Table 3); the k_{ch} values thus obtained revealed the high tendency of NQ to reduction at PANI.

Figure 7a' shows that the limiting current values I_L (and decrease in I_L^{-1}) are increased with the PANI-ClO₄ thickness. This increase is most possibly related to an increase in available sites for NQ reduction with thickness increment. At PANI-SO₄ (Fig. 7b') and PANI-Cl (Fig. 7c')-modified electrodes, an increase in limiting current (decrease in I_L^{-1}) is observed, but with further increase in thickness of film, a decrease in limiting current was observed.

It can be assumed that different real surface areas can be obtained for PANI films synthesized from solutions containing the different dopanting ions, and consequently,

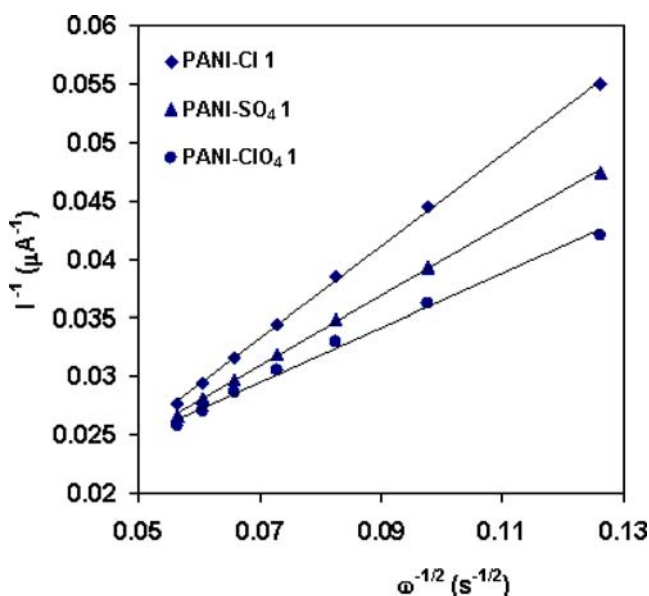


Fig. 8 Comparison between the variation of limiting current obtained for various PANIs with the same thickness for reduction of 5.6×10^{-4} M NQ at related acidic medium (1 M of HClO₄, H₂SO₄ and HCl) at $\nu=4 \text{ mV s}^{-1}$ and $\omega=1800 \text{ rpm}$

the degree of available EM reaction sites available will be different. (With increase in PANI-ClO₄ thickness, more reaction sites were created, but in PANI-Cl and PANI-SO₄, conductivity decrease and limiting current was decreased.

The Koutecky-Levich plots obtained for the three PANIs with the same PANI film thickness, shown in Fig. 8, revealed that, at lower rotation speeds, the limiting current is increased in the order PANI-Cl < PANI-SO₄ < PANI-ClO₄. With increasing rotation speed, the limiting currents approach each other with different slopes, so that infinite rotation speed gives the same value.

Conclusion

The polymerization of aniline on Pt electrode gives rise to the formation of a relatively stable deposited film. This film exhibits an electrocatalytic behavior towards the redox behavior of NQ due to reducing ΔE_p and increasing the NQ/H₂NQ redox couple reversibility. The nature of dopant anion was found to influence the ΔE_p and the separation of NQ redox peaks. In PANI electrodedoped with Cl⁻, an overlap between oxidation peaks of NQ and PANI was observed, while the PANI-modified electrodes electrodedoped with SO₄²⁻ at low scan rates and ClO₄⁻ resulted in a clear peak separation at the studied scan rates. A comparison between the RDE voltammograms of the PANIs and a bare Pt electrode clearly revealed a decrease in NQ reduction potential and an increase in the current-potential slope in RDE measurements for the PANI-modified electrodes. These evidences and a decrease in the corresponding ΔE_p values emphasize on acceleration of reaction and electrocatalytic effect of PANI electrodes. It was shown that the limiting current for different thickness of PANI films depend strongly on the nature of the dopant anion. At PANI-ClO₄-modified electrode, an increase in thickness of film resulted in an increase in the limiting current, while at other modified electrodes, a decrease in limiting current was observed with further increase in polymer thickness.

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