

Dopant Induced Effect on Electrocatalytic Reduction of Nitrobenzene Using Conducting Polypyrrole Thin Film Electrodes

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ABSTRACT: Conducting polypyrrole electrodes were prepared by electrochemical polymerization of pyrrole on vacuum-metallized glass substrates. These electrodes were modified by doping with a range of metal halides as dopant ions having different electronegativity. Electrochemical reduction of nitrobenzene using these electrodes was studied by means of cyclic voltammetry technique in acetonitrile medium containing aqueous HClO₄ (0.1M) as supporting electrolyte. It was found that the electronegativity of the dopant ion played a very important role in the electrocata-

lytic activity. Polypyrrole doped with nickel chloride gave the highest anodic current at the reduction potential of nitrobenzene. The results were explained on the basis of charge transfer efficiency at the electrode–electrolyte interface, which was associated with the acceptor state created by the dopant in the semi-conducting polymer. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 719–724, 2011

Key words: conducting polymer; charge transfer; polypyrrole; doping; electrocatalysis; nitrobenzene; reduction

INTRODUCTION

Conducting polymers have been studied extensively in the recent years for various applications such as electrochromic devices, electroluminescent/light emitting devices, chemical sensors, EMI/RF shielding, biosensors, corrosion resistance material, catalyst, etc.^{1–6} Conducting polymers, such as polypyrrole (PPy), polyaniline (Pani), polythiophene (PT), etc., can be used as catalyst due to their ion and electron conductivity, and these materials show excellent reversible redox behavior.^{7–14} These are sufficiently stable under experimental conditions employed, permeable to electroactive species, and are conductive enough for current flow among the solution, the electrocatalyst, and the current collector. The advantages of using such materials as catalyst lies on the fact that these are easy to coat on various substrate and have large reactive surface area because of their fibrillar nature.

It was earlier reported by our group that conducting polypyrrole doped with PdCl₂ shows catalytic activity toward methanol electro-oxidation and the catalytic activity increases several times when these films were modified by ion beam irradiation.¹⁵

Better catalytic activity in case of irradiated film samples were explained on the basis of better complexation between Pd and nitrogen atom of PPy chain.

We also reported in one of our previous communications, the electrochemical oxidation of methanol by conducting PPy doped with a series of metal halide dopants having different electronegativity such as ZrCl₄, NiCl₂, CuCl₂, etc. We showed that electronegativity of the dopant ions played an important role in the electrocatalytic activity of the modified PPy electrodes toward methanol oxidation. PPy film electrodes doped with lower electronegative metal halides showed better electrocatalytic activity toward methanol oxidation as compared to the one with higher electronegative metal halides. The results of this observation was explained on the basis of charge transfer efficiency at the electrode–electrolyte interface using energy level diagram.¹⁶

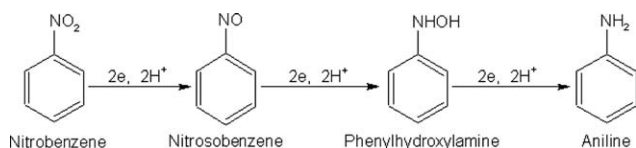
It is known that the charge transfer process from electrolyte to electrode/electrode to electrolyte is the key factor in the electrocatalytic oxidation/reduction process. The extent to which this transfer takes place determines the rate of the reaction. The level of the electrode and the reactant in the energy level, therefore plays main role in deciding activity/selectivity of the electrode. In this work, electrochemical reduction of nitrobenzene was carried out using modified conducting polypyrrole to study the effect of above factors in the reduction process. Modification of PPy

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films were done by doping with metal halide dopants having different electronegativities such as $ZrCl_4$, $NiCl_2$, $CuCl_2$, etc. Such films were found to exhibit a high electro-catalytic activity for nitrobenzene reduction. Relation of electrocatalytic activity toward reduction process and electronegativity of the dopant ions was established. Present investigations showed, polypyrrole films doped with $NiCl_2$ exhibits maximum catalytic activity toward nitrobenzene electro-reduction.

The reduction process of nitro aromatic compounds is of considerable interest because these are common groundwater contaminants and reduction reactions can play an important role in keeping the environment clean. Sources of nitro aromatic contaminants are explosives, dyes, agrichemicals, pesticides, etc. In the year 1898, F. Haber for the first time studied the electrochemical reduction of nitrobenzene. Haber used platinized platinum electrode for the electrochemical reduction of nitrobenzene.¹⁷

Reduction products of nitrobenzene are nitrosobenzene, phenylhydroxylamine, aniline, and coupled products such as azoxy-, azo-, and hydrazobenzene. The course of reactions varies depending on the choice of electrode material, electrode potential and electrolyte solutions, etc.



(1)

Various reports have been found in the literature about the reduction of nitrobenzene at various electrodes mainly Pt, Ni, Cu, etc.^{18–22} Reduction of various organic molecules on modified conducting polymers are also found^{23–26} but there is very less reference found in the literature on using conducting polymer electrodes for electrochemical reduction of nitrobenzene.^{27–29}

EXPERIMENTAL

Preparation of conducting polymer electrodes

The conducting polypyrrole (PPy) coated thin film electrodes were prepared on gold-coated glass plates by electro-polymerization method in a single compartment three electrode cell connected to computer controlled potenti-galvenostat (EC2010 Lab India) by standard conventional route.³⁰ Polymerization of pyrrole was carried out on gold-coated (vacuum deposited) glass plates in an aqueous electrolyte containing 0.1M pyrrole and 0.1M sulphuric acid with

platinum foil of 1 sq cm as counter electrode by applying 0.7V [vs. SCE (Standard Calomel Electrode)] constant potential for 120 s when PPy films (about 0.5 μm thick) got deposited. The PPy films were rinsed in distilled water, dried, and then dipped in 1M NH_3 solution for 30 min in order to un-dope them completely. These films were again rinsed in distilled water and dried. These undoped PPy films were then modified by doping with desired metal halide dopants viz $PdCl_2$, $CuCl_2$, $NiCl_2$, $MnCl_2$, $CoCl_2$, $FeCl_3$, and $ZrCl_4$ by placing them in the respective salt solutions ranging from 0 to 20 mM (slightly acidic with 2 mM HCl in case of $PdCl_2$) for 30 min followed by draining the excess liquid and drying.

Electrocatalytic reduction of nitrobenzene

The electrocatalytic activity of the PPy thin film electrodes was investigated using cyclic voltammetry technique as described elsewhere.^{15,16} In the electrocatalytic reduction of nitrobenzene process, PPy films were used as working electrode, platinum foil (Pt) of 1 sq cm area as counter electrode and SCE (Standard Calomel Electrode) was used as reference electrode. Cyclic voltammograms (CVs) were recorded at a scan rate of 30 mV s^{-1} from -1500 mV to $+1500$ mV in a three-electrode cell (described earlier) in acetonitrile medium containing aqueous 0.1M $HClO_4$ as supporting electrolyte and nitrobenzene as reactant. The electrolytic solution was purged with nitrogen for 20 min before every run. Nitrobenzene concentration was varied from 0.01M to 0.1M in each case.

Measurement of electrical properties

For measuring the electrical properties, PPy powder was synthesized by conventional chemical route using $FeCl_3$ (0.1M) as oxidizing agent.^{31,32} This PPy powder was first completely undoped by treating with 2M ammonia for 1 h and then redoped with different metal halide doping agents by placing them in the respective salt solutions ranging from 0 to 20 mM (slightly acidic with 2 mM HCl in case of $PdCl_2$) for 1 h followed by draining the excess liquid and drying. The PPy powder doped with different dopants was compression moulded at an applied pressure of 3 tons for 2 min to make pellets. The temperature dependence of conductivity for these pellets was measured using Keithley electrometer (614) in the range of 30° to 90°C. The activation energy for conduction was then estimated from these data by curve fitting procedure. The details of these experiments were same as described in earlier reports.^{33–35}

TABLE I
Table of Different Metal Halide Dopants with Their Electronegativities and Activation Energies of PPy Modified with Different Metal Halide Dopants (Position of Dopant Ion Impurity Levels in PPy Energy Gap)

Dopant ions	Electronegativity of dopants	Activation energy for conduction (eV)
ZrCl ₄	1.2	0.25
PdCl ₂	1.4	0.26
MnCl ₂	1.6	0.32
FeCl ₃	1.6	0.38
CoCl ₂	1.7	0.35
CuCl ₂	1.8	0.40
NiCl ₂	1.8	0.41

RESULT AND DISCUSSION

Measurement of electrical property

The temperature dependence of conductivity for the compression moulded pellets was measured in the temperature range of 30 to 90°C. The increase in conductivity with temperature is obvious for conducting polymer, which is due to thermal excitation process of charge carriers. The activation energy (ΔE) for conduction was then estimated from the Arrhenius plots of these data using curve fitting procedure and slopes of the linear portions of the graphs.

The ΔE values for different modified PPy powders are presented in the Table I. It could be seen in the table that activation energy (ΔE) value was less in case of PPy doped with NiCl₂, CuCl₂ whereas it was high in case of PPy doped with ZrCl₄. If one looks carefully, it was observed that the activation energy of doped PPy powders was inversely related to the electronegativity of the dopant ions, i.e., for PPy doped with higher electronegative transition metal salts activation energy was lower and for lower electronegativity it was higher. In the present case of doping, it should be pointed out that although all the salts contain Cl⁻, the doping salt used has profound effect on the properties of the semiconducting polymer. This can happen only if there is complex formation (donor/acceptor type) between the polymer and salt as a whole rather than only type of ion.³⁶⁻³⁹ Thus the concept of impurity levels in semiconducting material appears to be more appropriate to describe these materials.

Conducting polymer thin film electrodes and their electro-catalytic activity towards nitrobenzene reduction

The conducting PPy-coated electrodes prepared by electrochemical deposition techniques and modified by doping were used for electrocatalytic reduction of nitrobenzene. Doping of the PPy thin film was

investigated by comparing the CV's of undoped PPy film with the doped PPy film. CV's were run in an electrochemical cell containing 150 mL distilled water and 0.1M H₂SO₄. The CV's for undoped PPy and PPy doped with ZrCl₄ were shown in the Figure 1 to show electrochemistry of these polymer films. A CV investigation could be indication of modification of the conducting polymer film. It was seen in the Figure 1 that the shape of the CV's for doped PPy was broad whereas the shape of the CV's for the undoped PPy was narrow. In the CV of doped PPy current value was more compared to the undoped PPy. The broad CV's in case of PPy-ZrCl₄ film may be due to doping or coordination of the transition metals to the nitrogen atoms of PPy. Higuchi et al. suggested interaction of polyaniline with CuCl₂ by CV study as it is known that wave shape in CV of any complex or doped conducting polymer system is broader.⁴⁰ In case of undoped PPy film, being nonconductive in nature showed less redox current while the PPy doped with ZrCl₄, being conductive showed more redox current also. In the present case of doping interaction of transition metals to the nitrogen atoms of PPy are considered to interact through a π -conjugate chain which resulted broad wave shape in the CV.

In the electrocatalytic reduction of nitrobenzene modified conducting PPy-coated electrodes were used as working electrode. Preliminary investigations on the modified PPy electrodes indicated that the dopant ion concentration of 6 mM was sufficient to give good electrocatalytic activity. Hence all experiments using PPy were carried out with 6 mM doping concentration. The Figure 2 shows CV's for undoped PPy coated electrode and PPy doped with CuCl₂ electrode for nitrobenzene electrocatalytic

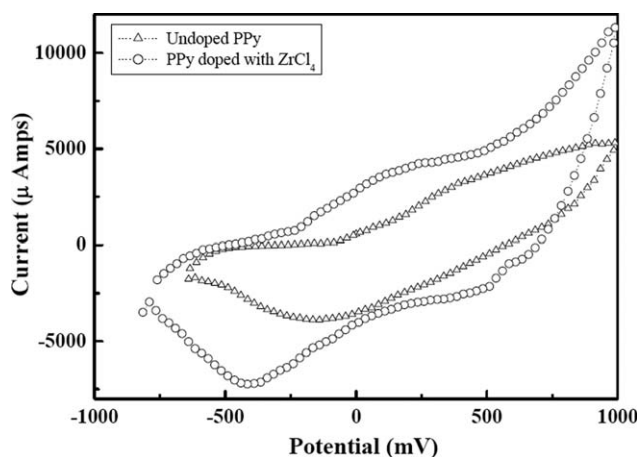


Figure 1 Cyclic voltammograms (CV) of undoped PPy film and the PPy film doped with ZrCl₄. CV's were run in electrochemical cell containing 150 mL distilled water and 0.1 M H₂SO₄ in presence of SCE reference electrode and Pt foil as counter electrode.

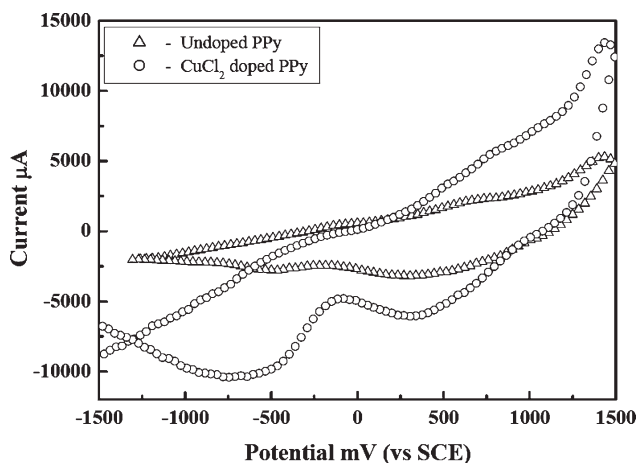


Figure 2 CVs of electrochemical reduction of nitrobenzene at undoped PPy and CuCl_2 doped PPy thin film electrodes. Nitrobenzene concentration in the electrolyte was 0.1M in acetonitrile medium in presence of SCE reference electrode and Pt foil as counter electrode.

reduction reaction. In the electrochemical reaction these electrodes were used as working electrodes, Pt foil as counter electrode and SCE as reference electrode. CVs were recorded from -1500 mV to $+1500\text{ mV}$ in acetonitrile medium containing aqueous 0.1M HClO_4 as supporting electrolyte and nitrobenzene as reactant. The electrochemical activity in these cases was clearly seen to enhance with the modification of electrodes as evidenced from the enhancement of current. The peak current at around -500 mV for CuCl_2 doped PPy electrode was almost four times higher as compared to the undoped PPy electrode. To identify the nature and origin of the cathodic current, the concentration of nitrobenzene (reactant) in the electrolyte was varied from 0.01M to 0.1M and the CV was recorded for each using NiCl_2 doped PPy-coated electrode, which were shown in Figure 3. It could be seen that there was a distinct peak appearing at the -500 mV (SCE) region and the cathodic current at this potential increased with the increase in concentration of nitrobenzene. Thus, the cathodic peak current at -500 mV is associated with the reduction of nitrobenzene, which is in agreement with electro-reduction potential reported for this reactant.^{41–43}

As already observed, PPy films modified by doping with transition metal halides showed good catalytic activity but the efficiency was dependent on the specific dopant. Hence it was essential to find out the most suitable dopant ion for the electro-reduction of nitrobenzene. Figure 4 was the CV's of the electrochemical reduction of nitrobenzene using PPy electrodes modified with different dopants viz. ZrCl_4 , PdCl_2 , MnCl_2 , FeCl_3 , CoCl_2 , NiCl_2 , and CuCl_2 . Reactant concentration in the electrolyte was 0.1M in each case. In the CV's, it could be observed that

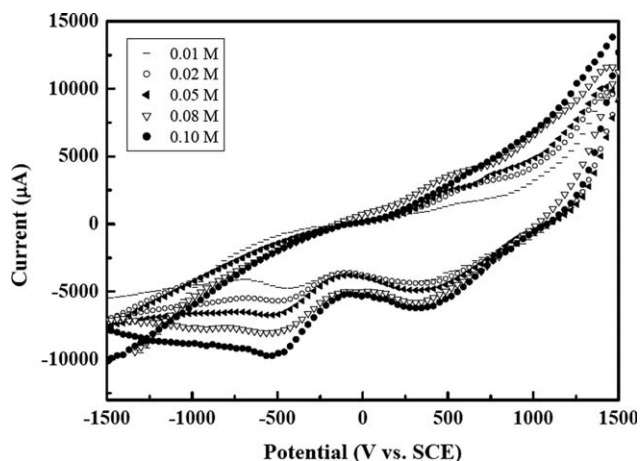


Figure 3 CV's of nitrobenzene electrochemical reduction with NiCl_2 doped PPy electrodes for varying reactant concentration (vs SCE). Curves with different symbols correspond to nitrobenzene concentrations of 0.01 – 0.1M .

there was a tremendous increase in peak current in the cathodic region for PPy films doped with NiCl_2 electrodes followed by CuCl_2 doped electrodes as compared to the undoped PPy film electrode. In all cases, there was a distinct peak appearing at about -500 mV (versus SCE) could be seen and the cathodic peak current at this potential increased for the dopant ions in the order $\text{ZrCl}_4 < \text{PdCl}_2 < \text{MnCl}_2 < \text{FeCl}_3 < \text{CoCl}_2 < \text{CuCl}_2 < \text{NiCl}_2$. When cathodic peak currents of these modified PPy doped electrodes was correlated with electronegativity of the dopant ions and a graph of cathodic peak current vs. electronegativity dopants was plotted a relation could be seen, which was shown in the Figure 5. From the graph, it was observed that higher electronegative dopant ions were catalytically more active toward electrochemical reduction of nitrobenzene as

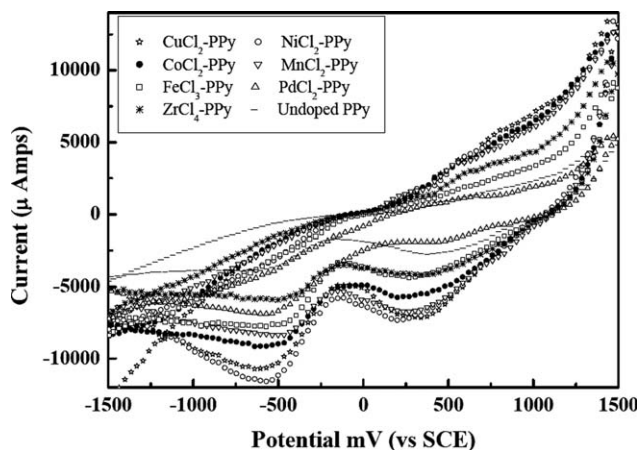


Figure 4 CV's of electrochemical reduction of nitrobenzene with PPy doped with different metal halide dopants (vs SCE). Curves correspond to 6 mM dopant concentration in PPy films at a scan rate of 30 mV s^{-1} in 0.1M HClO_4 and 0.1M nitrobenzene in acetonitrile.

compared to the lower electronegative dopant ions, i.e., with increase in electronegativity of the dopant ions catalytic activity increases. This clearly illustrated the role of the dopants in the catalytic efficiency of the PPy electrodes.

Conducting PPy films are known to exhibit some catalytic activity for electro-reduction of a few organic compounds, which is mainly associated with its redox behavior and charge transfer characteristics at the electrode | electrolyte interface. The electrocatalytic behavior of any material depends on various factors such as (a) the position of the energy levels involved for the reactive species and the electrode material; (b) charge transfer process across the interface of electrode and electrolyte; (c) diffusion of the reactants into/near the electrode surface; and (d) surface morphology of the electrode. In the present case, factors (a) and (b) are considered to be most relevant. Here PPy, being a p-type semiconductor, the results may be explained on the basis of electrochemical reactions at semiconductor electrode.

To investigate the reason for the better catalytic activity of the PPy modified with higher electronegative dopant ions toward nitrobenzene electro-reduction process, energy level of the each dopant ions with respect to PPy was plotted. Position of energy level with respect to the valence/conduction band was estimated from the activation energy for conduction (in eV) calculated earlier and presented in Table I. Since PPy is a p-type material the impurity doping level would be situated above the uppermost valence level. The energy level representation for these electrodes with respect to PPy in contact with nitrobenzene containing electrolyte and gold backing layer was depicted in Figure 6. Since the electrode was in cathodic condition, it was rich in electrons and transfer of electrons from electrodes to the elec-

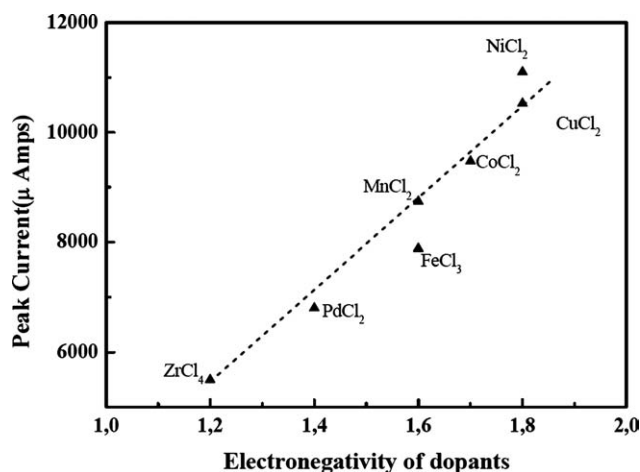


Figure 5 Graph of peak current for electro-reduction of nitrobenzene vs. electronegativity of the metal halide dopants. Dopant ion concentration is same in all cases (6 mM) with all other conditions as in Figure 4.

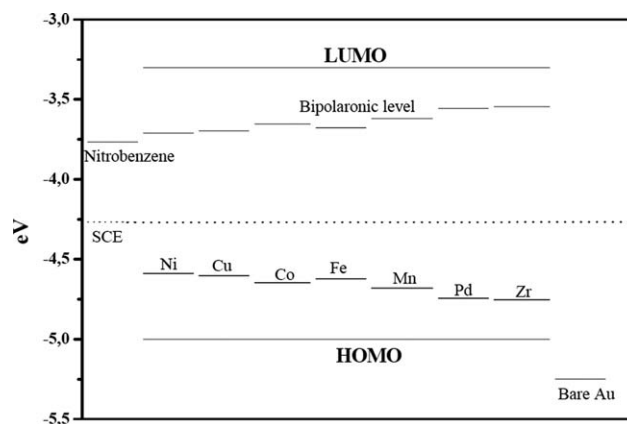


Figure 6 Energy level representation of the different modified PPy thin film electrodes in contact with nitrobenzene containing electrolyte. The difference between the impurity energy level and top of valence band was derived from activation energy data.

trolyte containing reactant took place leading to reduction process. It was seen in the energy level diagram that for PPy doped with NiCl₂ electrodes, it was easier for electrons to be transferred from the electrode to the reactant nitrobenzene than in other cases. It is thus clear that the charge transfer at the electrode/electrolyte interface is the most dominant factor in the present case which governs the electro-reduction of nitrobenzene using semi-conducting polymer electrode. In one of our previous communications, we showed the role of charge transfer process across electrode–electrolyte interface in electro-oxidation of methanol using conducting polymer thin film electrode. In the electro-oxidation process, the electrode is in the anodic condition and electron transfer takes place from electrolyte and these electrons combine with holes in the semiconductor.¹⁶ It may be mentioned here that such charge transfer processes are important for other effects such as electrochromism, photo-electrochemical effect, etc., which have been reported recently.^{44,45}

In the electrochemical reduction of nitrobenzene, the primary rate-determining step appears to be controlled by the charge transport at the cathode. From the aforementioned discussions, it is observed that conducting PPy electrodes modified with metal halide dopants can be used as electrocatalyst for electrochemical reduction of nitrobenzene and the position of energy level of the dopant ions in the polymer appear to play an important role in determining the electroreduction process using conducting polymer.

CONCLUSION

From all the aforementioned studies, it could be predicted that modified conducting PPy films

are electrocatalytically active toward nitrobenzene reduction reaction. Dependence of height of peak current with reactant concentration in the cathodic region confirms the forward nature of the reaction. PPy alone also showed some catalytic activity but when it was modified by doping with transition metal halides, the catalytic activity got enhanced. Electronegativity of the dopants play an important role in the catalytic activity of the conducting polymer electrode. The enhancement in the electrocatalytic activity was more pronounced in case of PPy electrodes modified with higher electronegative dopants as compared to the PPy films modified with less electronegative dopants. With the help of energy level diagram for the different dopant ions with respect to PPy in contact with the reactant nitrobenzene, the mechanism of electron/hole transport process in the electrochemical reduction process is explained. It was seen that in the reduction processes, for PPy doped with NiCl_2 electrodes, it was easier for holes to be transferred to the electrode from the reactant than in other cases. The hole transport to the electrode or electron transport from the electrode leads to the reduction of nitrobenzene to the desired products. Thus energy level of the electrodes and charge transfer process across the electrode/electrolyte interface appears to be the main factor which determines the rate of the reaction.

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