

Short communication

Role of dopant ions in electrocatalytic oxidation of methanol using conducting polypyrrole electrodes

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Abstract

Conducting polypyrrole electrodes obtained by electro-polymerization of pyrrole on vacuum metallized glass substrates are modified by doping with a range of metal halides as dopant ions having different electronegativity. Electro-oxidation of methanol using these electrodes is studied by means of cyclic voltammetry in 0.1 M HClO₄ as supporting electrolyte. It is found that the electronegativity of the dopant ion plays a very important role in the electrocatalytic activity. Polypyrrole doped with zirconium chloride gives the highest anodic current of 10 mA cm⁻² at the oxidation potential of methanol. The results are explained on the basis of the charge-transfer efficiency at the electrode|electrolyte interface, which is associated with the acceptor state created by the dopant in the semi-conducting polymer.

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1. Introduction

There is an increasing interest in the electro-oxidation of methanol because with respect to the development of direct methanol fuel cells (DMFCs). Precious metals such as Pt, Ru, Au and Pd dispersed in a conducting matrix such as carbon or graphite are commonly used as catalysts for the electro-oxidation of methanol. These are very expensive, however, and also experience problems due to carbon monoxide adsorption, which causes passivation of the catalytic surface [1–4]. Further, such electrodes are not easy to fabricate due to the high carbon/graphite concentrations that are required for conductivity. Hence, conducting polymers, a new class of electrode materials, are of considerable interest in the field of electrocatalysis. For examples, polymer coated electrodes and their modifications have been investigated [5]. The conducting polymers offer great advantages over other materials since they are permeable to electroactive species,

easily modified by different techniques, and easy to coat on various substrates.

We have reported previously [6] that conducting polypyrrole (PPy) films doped with PdCl₂ display catalytic activity towards methanol electro-oxidation, moreover, the catalytic activity increases several times when these films are subjected to ion-beam irradiation, which gives better complex formation. Given that the charge-transfer processes at the electrode|electrolyte interface are important in all these polymers, it is considered that the exact role of the doping agent should be investigated in detail. Accordingly, PPy films doped with a series of agents such as ZrCl₄, NiCl₂ and CuCl₂ have been studied for the electro-oxidation of methanol and a correlation of electrocatalytic activity with electronegativity of the dopant ions has been established in the present communication.

2. Experimental

Conducting polymer-coated electrodes were prepared by electro-polymerization of pyrrole in a single-compartment, three-electrode cell that was connected to computerized

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potentio-galvanostat (EC2010 Lab India) [7]. Pyrrole polymerization was carried out on gold-coated (vacuum deposited) glass plates in an aqueous electrolyte containing 0.1 M pyrrole and 0.1 M sulfuric acid with a platinum counter electrode. A constant potential of 0.7 V (versus a saturated calomel electrode, SCE) was applied for 120 s to deposit the PPy films (about 0.5 μm thick). The films were rinsed in distilled water, dried and then dipped in 1 M NH_3 solution for 30 min in order to de-dope them. The films were then doped with the desired doping agents, e.g., PdCl_2 , CuCl_2 , ZrCl_4 , by placing them in the respective salt solutions at concentrations that ranged 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. The electrocatalytic activity of the films was studied as described elsewhere [6]. Cyclic voltammograms (CVs) were recorded at a scan rate of 30 mV s^{-1} in a three-electrode cell (described above) with aqueous 0.1 M HClO_4 as electrolyte and methanol (MeOH) as the reactant. The electrolytic solution was enriched with oxygen by bubbling it with pure oxygen for 20 min prior to every run.

For measuring the electrical properties, PPy powder was synthesized by the conventional chemical route using FeCl_3 (0.1 M) as the oxidizing agent [8,9]. The PPy powder was first treated with 2 M ammonia for 1 h and then re-doped with different doping agents in the same manner as described above. The doped PPy was compression moulded at an applied pressure of 3 t for 2 min. The temperature dependence of the conductivity of these pellets was measured with a Keithley electrometer (614) in the range of 30–90 °C. The activation energy for conduction was estimated from the resulting data by a curve-fitting procedure. The details of these experiments were same as described in earlier reports [10–12].

3. Results and discussion

Preliminary studies on the modified PPy electrodes indicated that the dopant ion concentration of 0.006 M was sufficient to give good electrocatalytic activity. Hence all further studies were carried out with this doping concentration. Cyclic voltammograms with the doped PPy films as the anode and 0.1 M HClO_4 as the electrolyte with 0.1 M MeOH are shown in Fig. 1. In all cases, there is a distinct peak appearing at about 300 mV (versus SCE) and the anodic current at this potential increases for the dopant ions in the order: $\text{ZrCl}_4 > \text{PdCl}_2 > \text{MnCl}_2 > \text{FeCl}_3 > \text{CoCl}_2 > \text{CuCl}_2 > \text{NiCl}_2$. The anodic peak is associated with the oxidation of methanol, as reported by others [6,13,14], and is confirmed in the present case from the dependence of the current on MeOH concentration. Cyclic voltammograms obtained with varying concentrations of methanol in the electrolyte, i.e., from 0.01 to 0.1 M, and using PPy films doped with PdCl_2 are shown in Fig. 2. It should be noted that PdCl_2 is an excellent catalyst for the oxidation of organic compounds. The data clearly indicate that the anodic current increases

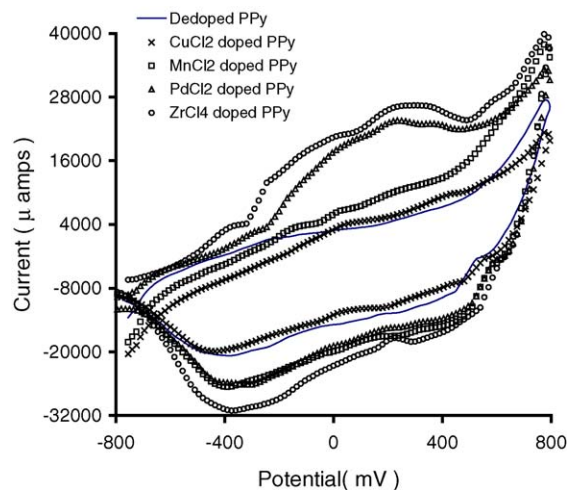


Fig. 1. Cyclic voltammograms (CVs) for electro-oxidation of methanol using PPy doped with different doping ions. Curves correspond to 0.006 M dopant concentration at a scan rate of 30 mV s^{-1} in 0.1 M HClO_4 and 0.1 M MeOH aqueous electrolyte.

with increase in the concentration of MeOH and hence the anodic wave is associated with the oxidation of MeOH . This reaction involves a large number of steps that yield different intermediate products, but finally results in the formation of carbon dioxide. Electron transport from electrolyte to electrode, or hole transport from electrode to reactant, leads to the oxidation of MeOH in the presence of O_2 , i.e.,



and so forth; finally CO_2

Conducting PPy films are known to exhibit some catalytic activity for the electro-oxidation of a few organic compounds [15,16]. This is mainly associated with its redox behaviour as well as the charge-transfer characteristics at the electrode|electrolyte interface. In the present investigation, a

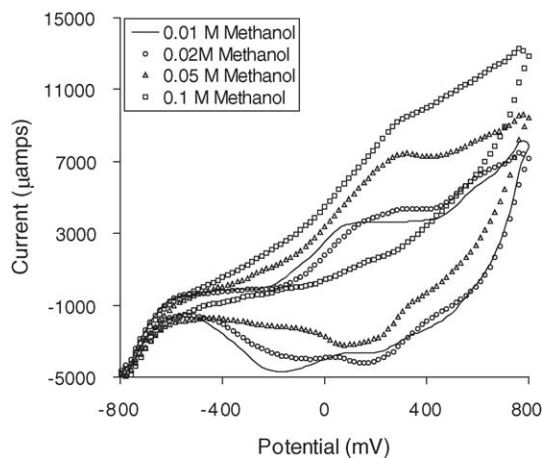


Fig. 2. Cyclic voltammograms of electro-oxidation of MeOH at PPy doped with 0.06 M PdCl_2 with increasing reactant concentration. Curves with different symbols correspond to MeOH concentrations of 0.01–0.1 M.

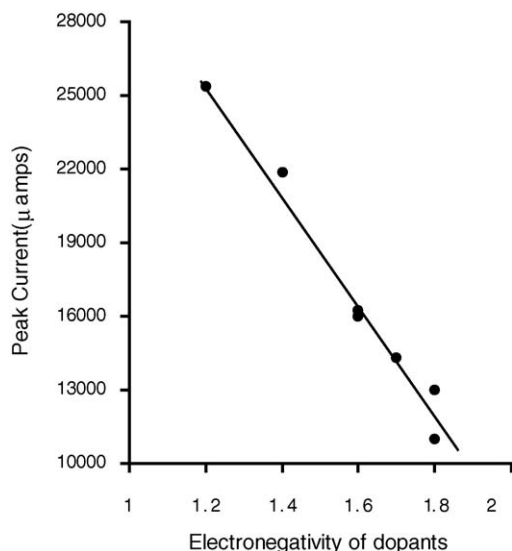


Fig. 3. Anodic oxidative current as function of electronegativity of dopant ion in PPY. Dopant ion concentration is the same in all cases (0.006 M) with all other conditions as in Fig. 1.

tremendous improvement in electrocatalytic activity is shown by the $ZrCl_4$ doped PPY electrode.

In order to establish a relationship between the nature of the dopant ion and its electro-oxidative efficiency, the peak current versus electronegativity of each of the dopant ions is plotted in Fig. 3. This clearly illustrates the role of the dopant in the efficiency of the PPY electrode, namely, a decrease in the electronegativity of the dopant ions causes an increase in the efficiency of the PPY film. The electrocatalytic behaviour of any material depends on various factors such as: (i) the position of the energy levels of the reactive species and the electrode material; (ii) the charge-transfer process across the electrode|electrolyte interface; (iii) the diffusion of the reactants into/near the electrode surface; (iv) the surface morphology of the electrode. In the present case, factors (i) and (ii) appear to be the most relevant. These results may be explained on the basis of electrochemical reactions at a semiconductor electrode. Here, PPY is considered as a p-type semiconductor. The electrical properties of PPY doped with different ions were measured in order to obtain the position of the impurity levels with respect to the valence/conduction band. From the temperature dependence of conductivity, the activation energy (in eV) was estimated for each sample; the results are listed in Table 1. The impurity doping level will be situated above the uppermost valence level since PPY is a p-type material. A representation of the energy levels of these electrodes with respect to PPY in contact with a MeOH-containing electrolyte and a gold backing layer is given in Fig. 4. Since the electrode is in an anodic condition, electrons are abstracted from the electrolyte and these combine with holes in the semiconductor. It is seen that for PPY doped with $ZrCl_4$, it is easier for electrons to be transferred from the reactant methanol to the electrode than in other cases. In the present study, it is therefore clear that charge transfer at the

Table 1
Position of dopant ion impurity levels in PPY energy gap

Dopant ions	Electronegativity	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

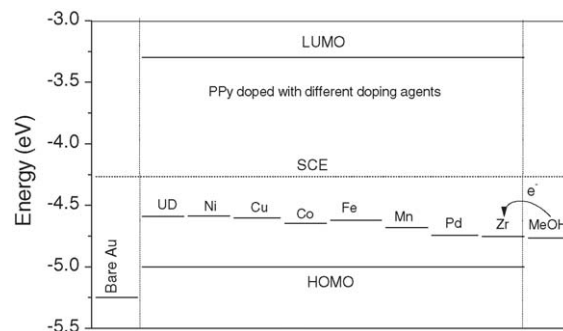


Fig. 4. Energy level representation for PPY with different dopants in contact with a MeOH-containing electrolyte. The difference between the impurity energy level and the top of valence band was derived from activation energy data.

electrode|electrolyte interface has the most influence on the electro-oxidation of methanol when using a semi-conducting polymer electrode. It should also be noted that such charge-transfer processes are also important in electrochromism and photo-electrochemical effects [17,18]. Despite the fact that Pt and Pd salts and their complexes are known to give good catalytic efficiency, the present findings indicate that there can be alternative dopants that also give large electrocatalytic activity and may prove to be more economical in many applications.

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