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Polypyrrole–palladium systems prepared in $PdCl_2$ aqueous solutions

Magdalena Hasik [a,*], Andrzej Bernasik [b], Anna Adamczyk [a], Grzegorz Malata [a], Kazimierz Kowalski [c], Józef Camra [d]

[a] *Department of Materials Science and Ceramics, University of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Kraków, Poland*
[b] *Physics and Nuclear Techniques, University of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Kraków, Poland*
[c] *Metallurgy and Materials Science, University of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Kraków, Poland*
[d] *Surface Spectroscopy Laboratory at University of Mining and Metallurgy, Joint Centre for Chemical Analysis and Structural Research, Jagellonian University, Ul. Reymonta 23, 30-059 Kraków, Poland*

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Abstract

In the work, reactions of a partially deprotonated polypyrrole doped with hydroxide ions (PPyOH) in various $PdCl_2$ aqueous solutions which differed in acidity were studied. Using X-ray photoelectron spectroscopy, X-ray diffraction and scanning electron microscopy it was established that in the $PdCl_2$ solutions of lower acidity PPyOH was oxidatively doped and Pd^0 and Pd^{2+} were incorporated into the polymer matrix. Pd^{2+} formed palladium(II) hydroxy-and/or aquochlorocomplex dopant anions and/or was coordinated by nitrogen atoms of the polymer (Pd–N bond). Additionally, deprotonation of PPyOH occurred in the $PdCl_2$ solutions of lower acidity. It was proposed that deprotonation of PPyOH was caused by nucleophilic attack of $[PdCl_3(H_2O)]^-$ on the positively charged, doped polymer chain. By comparison of the PPyOH and chloride-doped polypyrrole (PPyCl)–palladium systems prepared in similar $PdCl_2$ solutions of lower acidity it was shown that the type of the counterion in the starting polymer has a decisive effect on the deprotonation process.

PPyOH was less reactive towards palladium species in the $PdCl_2$ solutions of higher acidity where $[PdCl_4]^{2-}$ was the dominant complex. PPy–palladium systems containing exclusively Pd^{2+} were obtained in this case. It was proposed that incorporation of palladium species in these conditions proceeded *via* an acid–base reaction or coordination of palladium ions by the polymer chain (Pd–N bond formation).

Results of the studies may serve as the basis for the preparation of a variety of polypyrrole-supported palladium catalysts.

Keywords: Polypyrrole; Palladium; Palladium(II) chlorocomplexes

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1. Introduction

Polypyrrole (PPy) is a conjugated polymer whose chemistry makes it possible to prepare compounds of various interesting properties. The most typical reaction of PPy is its doping, i.e. oxidation which results in the formation of the positively charged (semioxidized) polymer chain and incorporation of dopant anions which compensate this charge.

PPy–transition-metal systems are of particular interest due to their potential applications as catalysts, sensors and biosensors, in photoimaging, etc. [1]. Such systems can be prepared using electrochemical or chemical methods.

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[*] Corresponding author. Tel.: +48-12-6173788; fax: +48-12-6331593.
E-mail address: mhasik@uci.agh.edu.pl (M. Hasik).

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Various anionic transition-metal complexes, such as $Au(CN)_2^-$, $(NiCN)_4^{2-}$ and of more complex structure have been incorporated into PPy as counterions during electropolymerization of pyrrole [1,2]. Reports on chemical preparation of PPy–transition-metal systems are rather scarce. It has been found that chemical reactions of PPy in chlorauric acid ($HAuCl_4$) solution lead to the oxidation of the polymer and formation of elemental gold [3]. This fact has been employed recently in the preparation of polypyrrole–gold composite colloids [4].

Palladium has been incorporated chemically into neutral PPy as well as neutral PPy/SiO_2 composites from $PdCl_2$ and $Pd(NO_3)_2$ acidic solutions; PPy–Pd systems obtained have been used as catalysts in hydrogenation of nitrobenzene [5,6]. These systems, however, have been characterized using mainly Pd 3d X-ray photoelectron spectra (XPS) which gave rather unclear results. Changes of the polymer chain as well as the chemistry of palladium(II) compounds in aqueous solutions have not been analyzed at all. Therefore it was difficult to propose the mechanisms of interactions between the polymer and palladium compounds. In the case of $PdCl_2$ in the experimental conditions studied (solution in 0.5 M HCl) it was postulated that $PdCl_2$ was incorporated into the polymer matrix. This—in fact—means that no chemical interactions occurred, which is not convincing. Moreover, use of environmentally unstable, neutral PPy is not a convenient way to prepare PPy-supported catalysts. In view of catalytic applications incorporation of palladium into the stable, doped PPy is much more advantageous.

Therefore our investigations have been concentrated on incorporation of palladium into the doped PPy. Preliminary results have shown that palladium can be introduced into PPy doped with chloride ions (PPyCl) as well as PPyCl treated with aqueous ammonia solution from $PdCl_2$ aqueous solutions containing HCl [7]. More detailed analysis of the XPS data of the PPyCl–Pd systems has lead us to the conclusions that several processes may take place in these systems [8]. Preliminary tests have also shown that PPy–Pd systems are catalytically active in hydrogenation of 2-ethylantraquinone [7].

The present work is focused on the studies of chemical reactions of the ammonia-treated PPyCl in a variety of $PdCl_2$ aqueous solutions containing HCl or/and KCl. These solutions differed in acidity and the dominant palladium(II) chlorocomplexes. Elemental analysis, X-ray diffraction (XRD), XPS, scanning electron microscopy, IR spectroscopy have been used to characterize the PPy–Pd systems obtained. The impact of the counterion in the polymer on the reactions with Pd^{2+} ions is discussed by comparison of the PPy–palladium samples prepared in similar $PdCl_2$ solutions using ammonia-treated PPyCl and PPyCl as starting polymers.

In the present paper interpreation of the processes taking place in the PPy–Pd systems based on the chemistry of palladium is proposed. The work has also an applicational aspect: using experimental conditions studied, it is possible to prepare a variety of PPy-supported palladium catalysts.

2. Experimental

2.1. Synthesis methods

Polypyrrole doped with chloride ions (PPyCl) was prepared by oxidation of freshly distilled pyrrole (10 mmol) with ammonium peroxodisulphate (2.5 mmol) in 1 M HCl solution (50 ml) at 0 °C. After synthesis, the resulting powder of PPyCl was washed with water and dried in dynamic vacuum at room temperature till constant mass.

PPyCl powder was stirred in the excess of 0.3 M aqueous ammonia solution for 7 h. In such a way, a partially deprotonated polymer (PPyOH) was obtained.

Polypyrrole–palladium systems were prepared by stirring the polymer powder at room temperature in the $PdCl_2$ aqueous solutions containing HCl and/or KCl for 72 h. Concentration of $PdCl_2$ in all the solutions was constant and equal to 2.29×10^{-3} M. Several series of experiments in which concentrations of HCl and KCl were varied in order to obtain various Cl:Pd molar ratios in the solutions were carried out. All the $PdCl_2$ solutions in which PPy–palladium systems were prepared in this study can be divided into two groups: of lower and of higher acidity. Their composition, pH values and maximum absorption in the visible light (λ_{max}) are collected in Table 1.

$PdCl_2$ aqueous solutions always contain a mixture of $[PdCl_n(H_2O)_{4-n}]^{2-n}$ (where $n = 1$, 2, 3 or 4) complexes. When KCl instead of HCl was added to the $PdCl_2$ solution its acidity (pH value) changed. Both, Cl:Pd and H^+:Pd molar ratios determine the type of palladium(II) chlorocomplexes that predominate in the solutions [9]. Thus, by using $PdCl_2$ solutions of different compositions we were able to study the influence of various palladium(II) chlorocomplexes on the reactions in the systems.

Spectra of the $PdCl_2$ solutions of lower acidity showed in the visible range the maxima at 430 nm (Cl:Pd molar ratio equal to 10) and at 465–470 nm (Cl:Pd molar ratio starting from 50, Table 1). The former one can be ascribed to the dominating $[PdCl_3(H_2O)]^-$ complex [10]. Since $[PdCl_4]^{2-}$ shows the maximum at 474 nm [10] it can be postulated that this complex prevailed in the solutions at higher Cl:Pd molar ratios with some contribution of $[PdCl_3(H_2O)]^-$. Additionally, low acidity of the solutions containing exclusively KCl (pH ranging from 3.98 to 5.97, Table 1) shows that hydrolysis of

Table 1
Composition, pH values and maximum absorption in the visible light (λ_{max}) of two groups of $PdCl_2$ solutions used for the preparation of PPy–Pd systems (in all the cases concentration of $PdCl_2$ was equal to 2.29×10^{-3} M)

Cl:Pd molar ratio	$PdCl_2$ solutions					
	Of lower acidity			Of higher acidity		
	Components (concentration [M])	pH	λ_{max}, nm	Components (concentration [M])	pH	λ_{max}, nm
10	HCl (1.81×10^{-2})	1.92	430	–	–	–
10	HCl (0.66×10^{-3}), KCl (1.76×10^{-2})	3.20	430	–	–	–
10	KCl (1.81×10^{-2})	3.98	429	–	–	–
50	KCl (0.11)	5.25	465	HCl (0.11)	1.30	465
100	KCl (0.22)	5.31	468	HCl (0.22)	1.09	468
200	KCl (0.45)	5.72	468	HCl (0.45)	0.79	473
439	KCl (1.00)	5.97	470	HCl (1.00)	0.41	474

some $[PdCl_3(H_2O)]^-$ present in these solutions yielding $[PdCl_3(OH)]^{2-}$ and H^+ took place [11].

$PdCl_2$ solutions of higher acidity exhibited maximum absorption at 465–474 nm (Table 1) which is due to the dominating $[PdCl_4]^{2-}$ complex. Low pH of these solutions was due to high HCl concentration.

2.2. Characterization methods

UV/VIS spectra of the $PdCl_2$ solutions used for the preparation of PPy–Pd systems were measured using a Hewlett Packard 8453 spectrophotometer.

Elemental analysis (determination of C, H, N, Cl) was performed using a Perkin-Elmer model 240 analyser. Determination of the contents of Pd in the PPy–Pd samples was carried out colorimetrically using the reaction of Pd^{2+} ions with KI [12] after dissolution of the samples in $HClO_4/HNO_3$ mixture.

XPS measurements were performed using a VSW Manchester equipment and AlKα radiation (1486.6 eV, 200 W). Operating pressure in the analytical chamber was less than 5×10^{-8} mbar. Carbon C 1s photoelectron peak originating from C–H or C–C group fixed at binding energy (BE) equal to 284.6 eV was used for calibration. Spectra of the same element were deconvoluted in the same manner. This made it possible to determine the differences in the shares of individual peak components in various samples. Spectra background was subtracted using Shirley method. Peaks were fitted with Gaussian–Lorentzian mix parameter fixed to 0.2. The N 1s spectra were fitted with four peaks of width (FWHM) equal to 1.7 eV. The Cl 2p spectra were fitted with three doublets (Cl $2p_{3/2}$–$2p_{1/2}$) with doublet separation (DS) of 1.7 eV and peaks width of 1.7 eV. The best fits of the Pd 3d spectra were obtained using three doublets (Pd $3d_{5/2}$–$3d_{3/2}$) with fixed area ratio equal to 3:2 and DS = 5.2 (exception for BE Pd $3d_{5/2}$ = 339.2 eV DS = 5.4). The Pd $3d_{5/2}$ peak width was equal to 1.8 eV.

FTIR spectra in the middle infrared range (400–4000 cm^{-1}) have been recorded in the transmission mode using a BioRad FTS60v spectrometer in KBr pellets. The resolution of the IR measurements was equal to 4 cm^{-1}.

XRD patterns of the powder samples were measured using a FPM SEIFERT XRD 7 diffractometer (nickel-filtered CuKα radiation).

Scanning electron microscopic (SEM) investigations were carried out on a Philips XL-30 microscope equipped with the X-ray microprobe.

3. Results and discussion

3.1. Characterization of the starting polymers

Samples of PPyCl before and after treatment with aqueous ammonia solution were characterized using IR spectroscopy, XPS, and elemental analysis. We were particularly interested in the chemical composition of the ammonia-treated polymer since the literature does not give a clear explanation on what happens when the doped PPy is treated with a base. Kang et al. [13] claim that this process results in the electrically neutral fully deprotonated PPy chain similarly to the deprotonation of polyaniline. Other authors suggest that the reaction of doped PPy with hydroxide ions involves a simple anion exchange, i.e. it leads to the formation of PPy doped with hydroxide ions [14,15].

Our results indicate that both PPy samples were doped. IR spectra of the polymers (Fig. 1) show a number of bands, among which the doping-induced ones at ~910 and ~1180 cm^{-1} [16] as well as a featureless broad absorption tail extending into NIR region (not shown in the figure) are clearly visible. A weak band at ~1700 cm^{-1} can be assigned to the stretching vibrations of the carbonyl group. Its intensity is similar in both

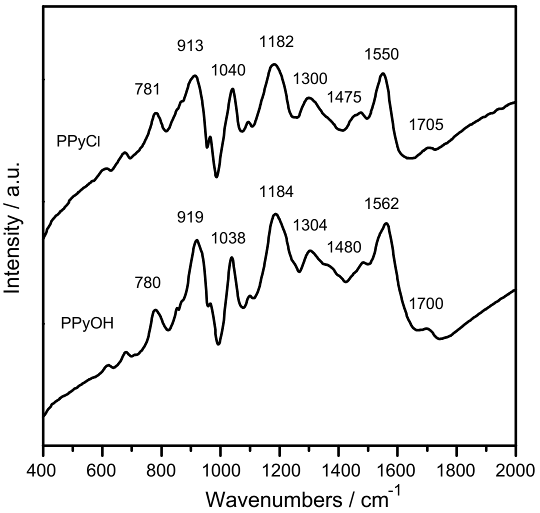


Fig. 1. IR spectra of PPyCl and PPyCl treated with aqueous ammonia solution (PPyOH).

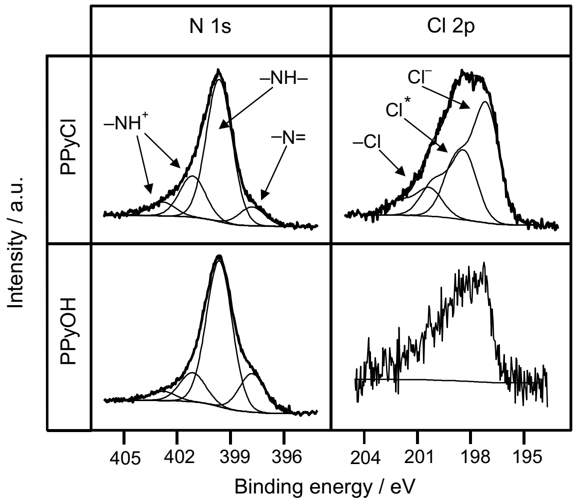


Fig. 2. N 1s and Cl 2p XPS spectra of PPyCl and PPyCl treated with aqueous ammonia solution (PPyOH).

spectra. This suggests that no new carbonyl defects have been formed in the polymer chain upon aqueous ammonia treatment.

N 1s XPS spectra of both PPy samples (Fig. 2, Table 2) contain high energy peaks corresponding to the doped nitrogen species (–NH$^+$–) [3,13,17,18]. The doping level (expressed as the share of –NH$^+$– groups in the polymer chain) of PPyCl is higher before than that after aqueous ammonia solution treatment.

The nature of the dopant anions in both PPy samples can be determined using elemental analysis and XPS. An analytical content of chlorine in PPyCl agrees fairly well with the doping level detected by N 1s XPS (Table 2). This indicates that chloride ions are counterions in this polymer. Similarly to other reports [18], however, the Cl 2p XPS spectrum of PPyCl (Fig. 2, Table 2) contains three doublets. Only one of them can be precisely ascribed to Cl$^-$ ions. The peak of the highest Cl 2p$_{3/2}$ BE is usually assigned to chlorine covalently bound to pyrrole ring (–Cl, Table 2) and indicates that substitution of some hydrogen atoms of the ring with chlorine has taken place. The origin of the intermediate component in the Cl 2p spectrum (Cl*, Table 2) is the least clear. It has been postulated, however, that this peak is due to Cl$^-$ ions in the positive environment present in the doped PPy [18].

As revealed by elemental analysis and XPS, which has shown a negligibly weak signal originating from Cl 2p, chlorine has been removed from PPyCl during treatment with aqueous ammonia solution (Table 2, Fig. 2). According to elemental analysis, both polymers contain oxygen which may be partly attributed to hydroxyl or carbonyl defects formed in the pyrrole ring during its oxidative polymerization [19]. The amount of oxygen is significantly higher in the ammonia-treated sample (Table 2). Hence, it can be concluded that the excess of oxygen detected by elemental analysis is associated with hydroxide counterions present in this polymer.

Table 2
Empirical formulae and results of deconvolution of N 1s and Cl 2p XPS spectra of PPyCl and PPyCl treated with aqueous ammonia solution (PPyOH)

Sample	Empirical formula[a]	XPS data: shares (%)					
		Binding energy [eV]			Binding energy [eV]		
		—N= 398.1	–NH– 399.7	–NH$^+$– 401.2, 402.9	Cl$^-$ 197.3	Cl* 198.4	–Cl 200.3
PPyCl	$C_4H_{3.13}NCl_{0.25}O_{0.33}$	9	66	25	55	32	13
PPyOH	$C_4H_{3.12}NCl_{0.01}O_{0.81}$	17	66	17	Very weak signal		

[a] Based on the results of elemental analysis. Contents of oxygen in the samples was calculated from the difference 100%—∑(C, H, N, Cl).

Additionally, the components due to imine-like nitrogen atoms (═N═) [3,13,17,18] can be distinguished in the N 1s XPS spectra (Fig. 2, Table 2). Their contribution is markedly higher in the spectrum of the ammonia-treated sample. This suggests that significant deprotonation of PPyCl has occurred. Since deprotonation involves exclusively transformation of –NH$^+$– to ═N═ groups, the share of the major component in the N 1s spectra of both samples corresponding to pyrrolyl nitrogen atoms (–NH–) [3,13,17,18] is unchanged (Table 2). It should be noted that ═N═ atoms detected by XPS in the PPyCl sample may be due to its deprotonation with water during washing after synthesis. They have been also observed by other authors [3].

It is interesting to note that the presence of deprotonated nitrogen atoms in the samples is not manifested in the IR spectra as clearly as in XPS. No distinct band originating from $>$C═N stretching vibrations which should appear at ~1600 cm^{-1} can be seen (Fig. 1). However, the band due to pyrrole ring skeletal vibrations at 1550 cm^{-1} [16] shifts significantly to higher wave-numbers in the IR spectrum of PPyCl treated with aqueous ammonia solution. This may be indicative of changes in the ring structure caused by deprotonation. More evident deprotonation detected by XPS suggests that this process occurs mainly on the surface of the sample.

Thus, based on the above results it can be concluded that the ammonia-treated PPyCl studied in our work has been a partially deprotonated PPy doped with hydroxide ions. Further on in this paper, this polymer will be referred to as PPyOH.

3.2. *PPy–Pd systems prepared in various $PdCl_2$ solutions*

We have found that the reactions of doped PPy are strongly influenced by the type of the $PdCl_2$ solution and—consequently—by the type of palladium(II) chlorocomplexes. This will be discussed in the subsequent sections.

3.2.1. *PPyOH–$PdCl_2$ solutions of lower acidity*

Two forms of palladium: Pd^0 and Pd^{2+} have been incorporated into the PPyOH matrix from all the $PdCl_2$ solutions of lower acidity. This has been evidenced by XRD, SEM and XPS studies.

XRD patterns of PPyOH–Pd samples (Fig. 3a) show distinct broad reflections centered at $2\Theta = 25°$ ($d = 0.35$ nm) and at $2\Theta = 10°$ ($d = 0.88$ nm) characteristic of the doped PPy structural features [2,20]. In addition, reflections at $2\Theta = 40°$ ($d = 0.22$ nm) and at $2\Theta = 46.6°$ ($d = 0.19$ nm), which originate from crystalline metallic palladium particles [21] are clearly seen.

In SEM micrographs (Fig. 3b) metallic palladium particles are visible as white spots. This has been established by X-ray microprobe analysis, which has shown that the spots contain exclusively palladium. Numerous metallic palladium agglomerates of various sizes (from 0.5 to 2 µm) are seen in the samples. Clearly, they form a separate phase in the systems.

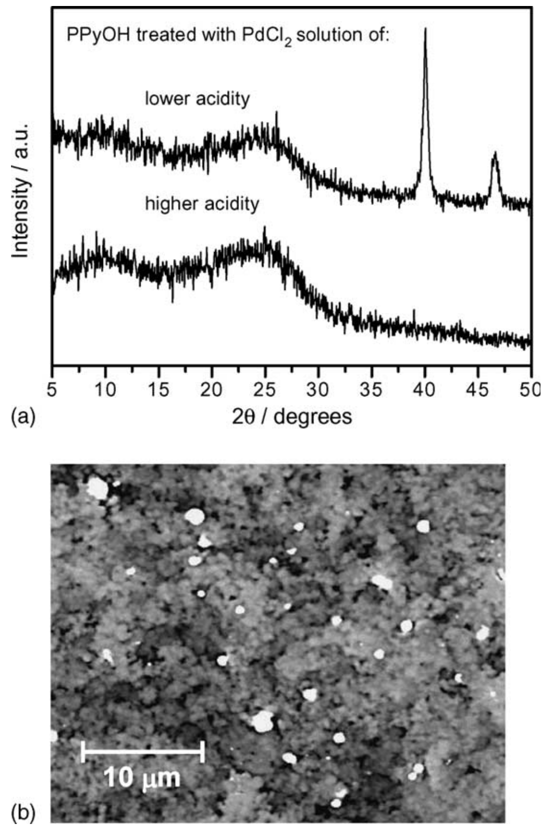


Fig. 3. (a) Typical XRD patterns of the PPyOH–Pd samples prepared in $PdCl_2$ solutions of lower acidity (0.11 M KCl) and of higher acidity (0.11 M HCl). (b) Typical SEM micrograph of PPyOH treated with $PdCl_2$ solution of lower acidity (1.81×10^{-2} M KCl).

Pd core level spectra (Fig. 4, Table 3) reveal the presence of Pd^0 in the samples as well. According to XPS, however, Pd^{2+} is the major palladium component.

Processes which result in the incorporation of both, Pd^0 and Pd^{2+} into the PPyOH matrix should be accompanied by relevant changes in the polymer chain. Thus, formation of Pd^0 is expected to proceed with simultaneous oxidative doping of the polymer, i.e. transformation of the –NH– groups to the –NH$^+$– ones. Quite unexpectedly, however, comparison of the N 1s XPS data of the starting PPyOH (Table 2) with those of PPyOH–Pd samples (Table 3) shows that the share of –NH– in the polymer chain decreases, but the contribution of –NH$^+$– is almost unchanged. Instead, the contents of ═N═ grow. This suggests that oxidative doping of PPyOH and further deprotonation of the polymer are competitive reactions which proceed simultaneously in these systems.

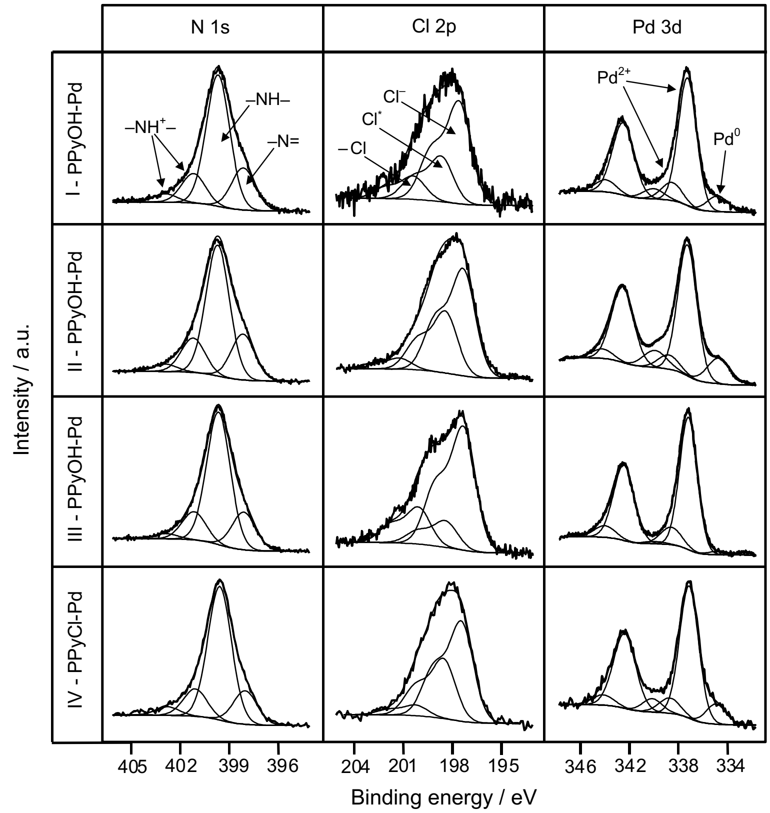


Fig. 4. N 1s, Cl 2p and Pd 3d spectra of selected PPy–Pd samples studied in the present work (total palladium contents in the samples: 0.04 moles Pd per 1 nitrogen atom in the polymer chain).

Deprotonation of PPyOH is schematically depicted in Fig. 5. It is most probably caused by the nucleophilic attack of $[PdCl_3(H_2O)]^-$ present in the solutions on the positively charged polymer chain. Since H_2O in the palladium(II) coordination sphere is easily exchanged with other ligands [11], its replacement by hydroxide ions from PPyOH seems to be the driving force for the polymer deprotonation.

Oxidative doping of PPy always leads to the incorporation of dopant anions into the polymer matrix. In the PPyOH–Pd samples their nature can be determined using Cl 2p and Pd 3d XPS (Fig. 4, Table 3). Cl 2p spectra suggest that Cl^- are the prevailing dopant anions. The intermediate peak (Cl^*) in the Cl 2p spectra of PPyOH–Pd samples can be, however, partly ascribed to chlorine atoms in palladium(II) chlorocomplexes [22].

Two components due to Pd^{2+} can be distinguished in the Pd 3d spectra. One of them is due to palladium in the Pd–Cl bond since $PdCl_2$ exhibits a maximum at similar BE [22]. The second Pd^{2+} peak is not so unequivocal. Oxygen-containing palladium compounds, such as palladium(II) acetate as well as nitrogen-containing palladium(II) complexes, such as $[Pd(NH_3)_4]Cl_2$ give maxima at similar BE [22]. Hence, this peak can be assigned either to palladium complexes containing OH^-, H_2O ligands or to the Pd–N bond.

Thus, the observed Pd^{2+} spectra imply that anionic palladium(II) complexes bearing Cl^-, OH^- and/or H_2O ligands are the counterions in the PPyOH–Pd samples. The scheme of oxidative doping in the systems studied is presented in Fig. 6.

Coordination of Pd^{2+} by N atoms of the PPyOH chain (i.e. Pd–N bond) is also possible. Formation of complexes between PPy and other transition metals, such as Au(I) [23], Au(III) [24] as well as Cu(I) [25] during electrochemical doping has been postulated.

3.2.2. PPyOH–$PdCl_2$ solutions of higher acidity

We have found that the amount of palladium incorporated into PPyOH drops with the increase in HCl concentration in the solution (Fig. 7). This suggests a strong influence of HCl on the reactions in the systems and indicates low reactivity of the polymer towards palladium(II) ions under conditions of higher acidity.

Exclusively Pd^{2+} has been introduced into PPyOH from the $PdCl_2$ solutions of higher acidity. No crystalline metallic particles are visible in the XRD patterns (Fig. 3a) and SEM micrographs of the palladium-con-

Table 3
Results of deconvolution of XPS spectra of PPy–Pd samples

Symbol	Starting polymer	Sample		XPS data: shares (%)								
		Synthesis conditions		N1s			Cl2p			Pd3d		
		HCl concentration [M]	KCl concentration [M]	Binding energy [eV]			Binding energy [eV]			Binding energy [eV]		
				–N=	–NH–	$-NH^+-$	Cl^-	Cl^*	–Cl	Pd^0	Pd^{2+}	
											Pd–Cl	Pd–O/N
				398.1	399.7	401.2, 402.9	197.3	198.4	200.3	335.3	337.8	339.2
I	PPyOH	–	1.81×10^{-2}	20	62	18	60	27	13	11	77	12
II	PPyOH	0.66×10^{-3}	1.76×10^{-2}	21	60	19	60	34	6	17	74	9
III	PPyOH	0.109	–	18	65	17	66	14	20	3	84	13
IV	PPyCl	0.66×10^{-3}	1.76×10^{-2}	16	64	20	58	35	6	12	78	10

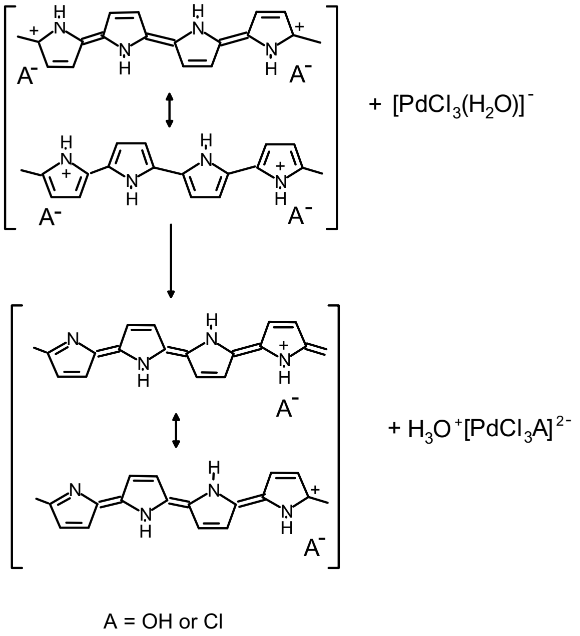


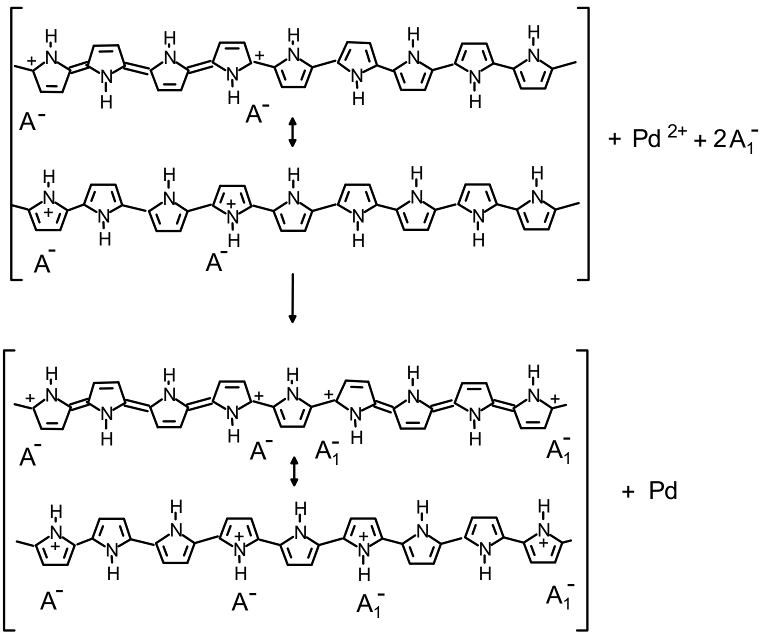
Fig. 5. Scheme of deprotonation of PPyOH and PPyCl in the presence of $[PdCl_3(H_2O)]^-$ (structures are not shown quantitatively).

taining samples. Pd 3d XPS spectra reveal a small amount of Pd^0 (Table 3), practically indistinguishable in the spectrum (Fig. 4). According to XPS (Table 3), Pd^{2+} forms Pd–Cl and Pd–O and/or Pd–N bonds similarly to the samples prepared in the $PdCl_2$ solutions of lower acidity (Section 3.2.1). Similar are also the components of Cl core level spectra, Cl^- being the dominant species (Fig. 4, Table 3). Very small changes with respect to the starting polymer in the N 1s XPS (Tables 2 and 3) confirm low reactivity of PPyOH towards palladium(II) ions in the conditions of high HCl concentration.

Based on the above, it can be concluded that the interactions between PPyOH and palladium(II) chlorocomplexes present in the $PdCl_2$ solutions of higher acidity do not involve oxidative doping of the polymer. Formation of Pd–N bond and/or acid–base reaction between H_2PdCl_4 (the dominant species in the solutions) and PPyOH chain can be postulated as the main reactions in these conditions. Even though PPy is a rather weak base (pK_a of C2 atoms = −3.8, pK_a of N atoms = −10 [26]), the acid–base type doping of this polymer has also been reported [27].

3.2.3. The influence of the acidity on the PPyOH–Pd^{2+} interactions

Acidity influences the reduction of Pd^{2+} to Pd^0. This can be easily established when PPyOH–Pd systems prepared in the $PdCl_2$ solutions of lower and higher



A = OH or Cl
A_1 = Cl or Pd-containing anions

Fig. 6. Scheme of oxidative doping of PPyOH occurring in the $PdCl_2$ solutions of lower acidity (structures are not shown quantitatively).

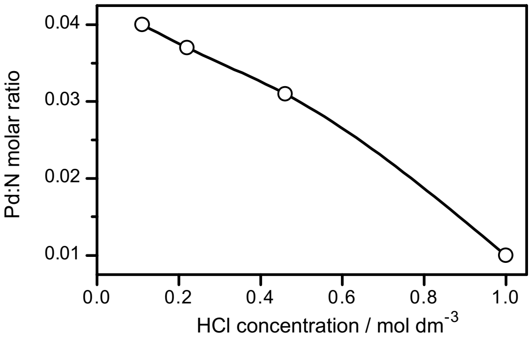


Fig. 7. Total Pd contents (expressed as the number of moles Pd per 1 nitrogen atom in the polymer chain) in the PPyOH–Pd samples prepared in the $PdCl_2$ solutions of higher acidity at different HCl concentrations. Starting ratio: 0.04 moles Pd in the solution per 1 nitrogen atom in the polymer chain.

acidity at the same Cl:Pd molar ratios (Table 1) are contrasted. Reduction of a fraction of Pd^{2+} to Pd^0 has occurred exclusively in the conditions of lower acidity. This may seem unexpected since $[PdCl_4]^{2-}$ has been the major complex in all these solutions. This complex should be difficult to be reduced in the solutions of high Cl^- concentrations.

There are two main differences in the composition of these two types of $PdCl_2$ solutions: presence of potassium cations instead of protons (Table 1) as well as formation of palladium(II) hydroxychlorocomplexes in the solutions of lower acidity (see Section 2.1). Since palladium(II) hydroxychlorocomplexes are reduced at lower potential than palladium(II) chlorocomplexes and palladium(II) aquocomplexes ($E^0_{\mathrm{Pd(OH)_2/Pd}} = 0.07$ V, $E^0_{\mathrm{[PdCl_4]^{2-}/Pd}} = 0.62$ V and $E^0_{\mathrm{[Pd(H2O)_4]^{2+}/Pd}} = 0.99$ V [11,28]) their contribution to the Pd^{2+} reduction process does not seem very probable. Hence, it can be postulated that introduction of potassium cations into the $PdCl_2$ solution facilitates the reduction of Pd^{2+} to Pd^0 in the systems studied.

In contrast, protons seem to inhibit the Pd^{2+} to Pd^0 reduction. Therefore this process does not occur in the solutions of higher HCl concentrations. Furthermore, low reactivity of PPyOH in these conditions clearly demonstrates that the redox process between the polymer and Pd^{2+} ions is necessary for higher reactivity.

3.2.4. The role of the counterion in the PPy–Pd^{2+} interactions

Comparison of the properties of PPyOH–Pd and PPyCl–Pd samples prepared in similar $PdCl_2$ solutions of lower acidity shed a light on the role of the counterion in the PPy–Pd^{2+} ions interactions.

As revealed by XRD, SEM and XPS, processes occurring in the PPyCl and PPyOH systems are similar: oxidative doping with simultaneous Pd^0 formation (Fig. 6), deprotonation (Fig. 5) and coordination of Pd^{2+} by N atoms of the polymer. Pd 3d XPS shows higher amount of Pd^0 in the PPyOH–Pd sample (Table 3). This indicates that PPyOH exhibits stronger reducing properties towards palladium(II) ions than PPyCl.

The type of the dopant anion in PPy influences deprotonation of the polymer caused by nucleophilic attack of $[PdCl_3(H_2O)]^-$ on the positively charged polymer chains. Deprotonation (measured as the proportion of —N= atoms in the N 1s XPS spectra with respect to the starting polymer) of PPyCl has been significantly higher than that of PPyOH (Tables 2 and 3). This can be explained by the fact that Cl^- are stronger ligands for Pd^{2+} ions than OH^- [11]. Hence, the replacement of H_2O in $[PdCl_3(H_2O)]^-$ by chloride ions from PPyCl is more efficient than by hydroxide ions from PPyOH. Consequently, PPyCl is deprotonated to a higher degree. It is important to note that in this process $[PdCl_3(H_2O)]^-$ is as strong nucleophilic agent as the aqueous ammonia solution. The contents of —N= atoms in the N 1s spectra of PPyOH (Table 2) and PPyCl–Pd sample (Table 3) are similar.

4. Conclusions

To summarize, we have prepared polypyrrole–palladium systems in two types of $PdCl_2$ aqueous solutions: of lower and of higher acidity. In the studies a partially deprotonated polypyrrole doped with hydroxide ions (PPyOH) has been used as the starting material. It has been found that different chemical reactions take place in various $PdCl_2$ solutions. They are as follows:

1. In the $PdCl_2$ solutions of lower acidity: oxidative doping of PPyOH and deprotonation of the polymer. As the result of oxidative doping, Pd^0 and Pd^{2+} in palladium(II) complexes containing Cl^-, H_2O, OH^- ligands as dopant anions are incorporated into the polymer matrix. Deprotonation may be caused by nuclephilic attack of $[PdCl_3(H_2O)]^-$ on the doped polymer chain. Coordination of Pd^{2+} ions by nitrogen atoms of the polymer (Pd–N bond formation) is also possible.
2. In the $PdCl_2$ solutions of higher acidity: coordination of Pd^{2+} ions by nitrogen atoms of the polymer (Pd–N bond formation) and/or acid-base reaction between H_2PdCl_4 (the dominant species in the solutions) and PPyOH chain.

Replacement of protons by potassium cations in the $PdCl_2$ solutions has beneficial effect on the reduction of Pd^{2+} to Pd^0 by the polymer. Additionally, it has been established that the degree of the deprotonation of the polymer depends on the type of the counterion present in polypyrrole. This has been found by comparison of the PPyOH–Pd and chloride-doped polypyrrole (PPyCl)–Pd systems prepared in similar $PdCl_2$ solutions of lower acidity.

Results of the studies may constitute a good starting position for the preparation of a variety of polypyrrole-supported heterogeneous palladium catalysts.

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