Study of deprotonation processes of polyaniline by differential multiwavelength Raman spectroscopy in an electrochemical system

Regina Mažeikienė,

Gediminas Niaura,

Albertas Malinauskas[*]

*Department of Organic Chemistry,
Center for Physical Sciences and Technology,
3 Saulėtekio Avenue,
10257 Vilnius, Lithuania*

A layer of polyaniline has been deposited at a gold electrode and studied by differential multiwavelength Raman spectroelectrochemistry. A set of laser line excitation wavelengths was used, including blue (442 nm), green (532 nm), red (633 nm) and far red (785 nm). From the results obtained, the difference spectra between deprotonated (pH 9.0) and protonated (pH 1.0) forms of oxidized and reduced polyaniline were derived and analysed. The characteristic features for different forms of polyaniline were identified, and their dependence on the excitation wavelength was shown. In addition to the usual Raman spectroscopy, the differential spectroscopy enables one to analyse the increase or decrease of intensity for selected Raman bands upon a reversible deprotonation of this polymer.

Keywords: polyaniline, Raman spectroscopy, differential spectra, spectroelectrochemistry, multiwavelength, redox processes, protonation

INTRODUCTION

Raman spectroscopy is a very useful tool for elucidating chemical processes taking place in conducting polymers, particularly in polyaniline. This technique allows one to identify structural changes occurring during chemical or electrochemical oxidation and reduction, and a reversible protonation in aqueous solutions of different acidity. The early works on Raman spectroscopy and spectroelectrochemistry of polyaniline and some related materials were done more than two decades ago [1–6].

These early works disclosed an interesting phenomenon, as applied to conducting polymers: excitation of Raman spectra with different laser lines results in different Raman features. Every single and well-defined form of polyaniline can show dif-ferent Raman features depending on the excitation wavelength. This phenomenon is based on different light absorption properties for a variety of polyaniline forms differing in their redox and protonation state. In an acidic solution, the reduced form of polyaniline absorbs in the near UV range at approximately 320 nm [7]. A stepwise electrochemical oxidation of a polyaniline layer placed at a transparent electrode leads to the appearance of a transition absorbance band around 420 nm, which disappears gradually by shifting the electrode potential to higher potentials, *viz.* by deeper electrooxidation of a polyaniline layer, and an intense absorbance band or a series of bands appear in the red range of spectrum beyond 600 nm by even deeper electrooxidation [7]. Accordingly, different Raman excitation wavelengths fall into resonance with different redox forms, and, as a result, different features are observed. It was shown that the blue laser line

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[*] Corresponding author. Email: albertas. malinauskas@ftmc.lt

excitation at 457 nm falls into resonance with a reduced form, thus, only characteristic features for this particular form are observed without any sensitivity towards the electrochemical oxidation [1]. As opposite, a strong resonance with the blue coloured oxidized forms leads to well-expressed features of these states of polyaniline at the 1064 nm NIR excitation [1]. Also, a strong resonance with the blue coloured oxidized forms was found for red (at 676 nm) and near infrared (at 1064 nm) excitations [2, 3]. The green excitation, performed at 488 nm and 514 nm, was reported to result in Raman features characteristic for all redox forms depending on the degree of oxidation [2].

In our previous works, we have studied the redox interconversions of different forms of polyaniline with the use of UV, blue and green [8], as well as red or near infrared excitations [9]. The present work has been aimed at the study of differently protonated oxidized and reduced forms of polyaniline by multiwavelength differential Raman spectroelectrochemistry.

EXPERIMENTAL

Like as in our previous works [8–11], a cylinder-shaped spectroelectrochemical cell was used in all experiments. A circular gold electrode of about 5 mm in diameter, attached to a Teflon rod holder, was used as a working electrode and was placed at a distance of approximately 2 mm from the cell optical window. During the experiments, the cell was periodically moved with respect to the laser beam using custom-built equipment [12]. As a counter and a reference electrodes, platinum wire and saturated Ag/AgCl electrodes were used, respectively. The electrode potentials reported below relate to this Ag/AgCl reference electrode. The gold working electrode was cleaned by etching in a mixture of 30% hydrogen peroxide and concentrated sulfuric acid, 3:1 by volume, then ultrasonicated in aqueous ethanol, and rinsed with water. The cell was driven by a BASi-Epsilon model electrochemical workstation (Bioanalytical Systems Inc., USA).

A layer of polyaniline was deposited at a gold electrode from a solution of 0.05 M of aniline and 0.5 M of sulfuric acid by applying a controlled electrochemical potential of 0.8 V for 20 min. As a working electrolyte, Britton–Robinson buffer solutions of pH 1.0 and pH 9.0, containing additionally 0.1 M of potassium chloride, were used.

Raman spectra were recorded with a confocal microspectrometer inVia (Renishaw, UK) equipped with a camera thermoelectrically cooled at –70°C CCD and a microscope. For excitation of the Raman spectra, the following lasers were used: a continuous-wave 442 nm (He-Cd laser, 4 mW, 2400 lines/mm grating), 532 nm (diode-pumped solid state laser, 3 mW, 1800 lines/mm grating), 632.8 nm (He-Ne laser, 1 mW, 1200 lines/mm grating) and 785 nm (diode laser, 4 mW, 1200 lines mm^{-1} grating). The 5×/0.12 NA objective lens was used for the excitation and collection of the Raman spectra excited with all laser lines.

RESULTS AND DISCUSSION

The structures of different forms of polyaniline discussed below are depicted in Fig. 1. A reduced non-protonated form, commonly known as leucoemeraldine base (LEB), contains benzene type rings separated by secondary aminogroups. Upon protonation, usually occurring in acidic solutions, a part of aminogroups become positively charged. Accordingly, charge compensation by auxiliary anions from the solution (An$^-$) occurs, leading to the reduced protonated form of polyaniline, known as leucoemeraldine salt (LES). Oxidation of either of these two reduced forms leads to the formation of quinone type rings. At a full oxidation, each second benzene ring turns into a quinone ring, resulting either in a non-protonated oxidized form, known as pernigraniline base (PNB), or in a corresponding protonated form, usually depicted as pernigraniline salt (PNS) (Fig. 1). There is a great deal of interest in partially oxidized forms, possessing a somewhat lower part of quinone rings in respect to benzene ones. Particularly, a partially oxidized protonated form that contains quinone and benzene rings at a formal ratio of 1:3, known as emeraldine salt, arises the greatest interest because of its unusual physical and chemical properties like electric conductivity.

Figure 2 shows the difference Raman spectra for the reduced and oxidized forms of polyaniline, as obtained at the 442 nm blue laser line excitation. Figure 2, as well as the next following Figures, shows generally two kinds of Raman features observed in difference spectra. The positive Raman bands show

LEB

LES

PNB

PNS
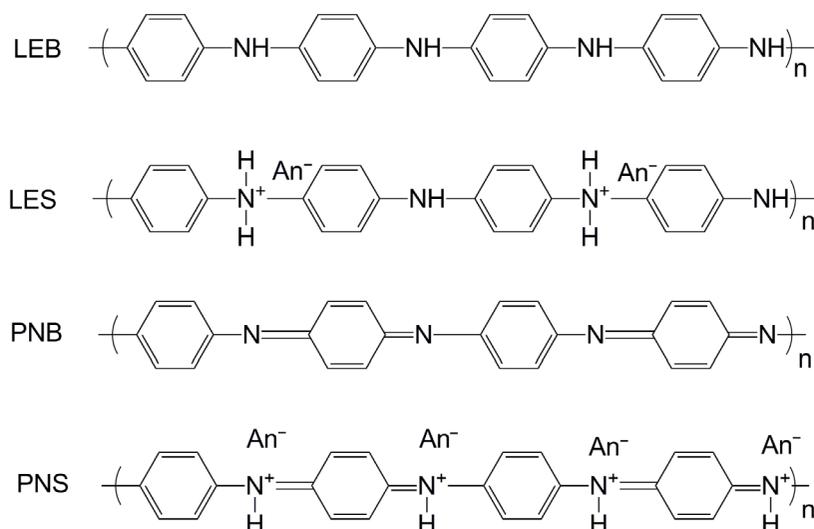
Fig. 1. Chemical structures of polyaniline: a reduced non-protonated leucoemeraldine base form (LEB), a reduced protonated leucoemeraldine salt form (LES), an oxidized non-protonated pernigraniline base form (PNB) and an oxidized protonated pernigraniline salt form (PNS)

442 nm excitation

Difference: Reduced form pH9.0–pH1.0

Difference: Oxidized form pH9.0–pH1.0

Raman intensity, arb.

1800   1600   1400   1200   1000   800   600   400

Raman shift, cm^{-1}
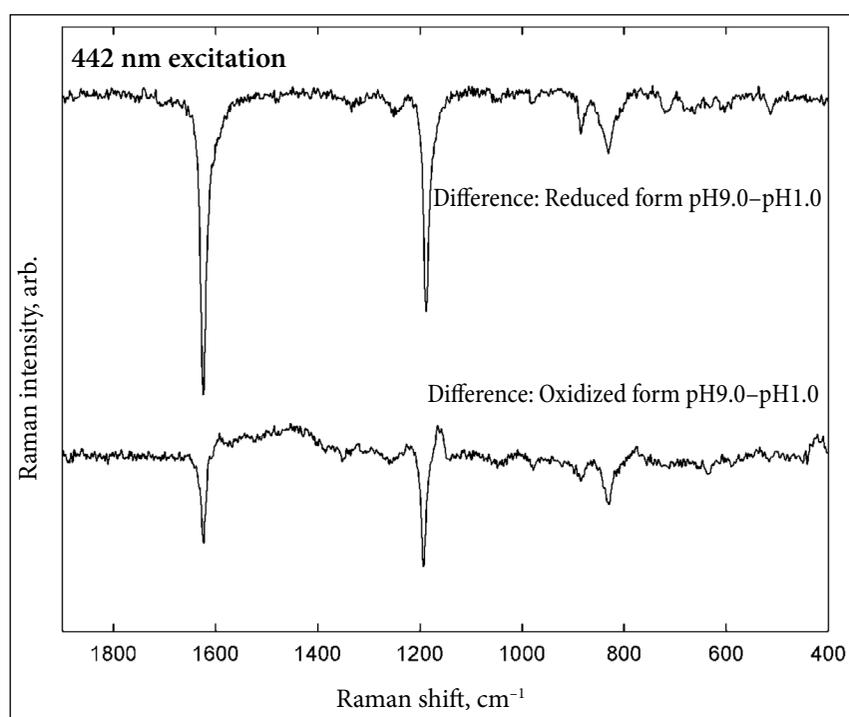
Fig. 2. Difference Raman spectra obtained at 442 nm laser line excitation wavelength for the reduced (top) and the oxidized (bottom) forms of polyaniline (as indicated) by subtracting the spectra recorded at solution pH 1.0 from those recorded at solution pH 9.0. Spectra for the reduced form were recorded at a controlled electrode potential of 0.0 V and −0.5 V for pH 1.0 and pH 9.0 solutions, respectively, and spectra for the oxidized form were recorded at a potential of 0.6 V and 0.1 V for solution pH 1.0 and 9.0, respectively

specific features that grow up upon deprotonisation of the corresponding form of polyaniline, *viz.* by dropping the solution acidity from pH 1 to pH 9. Adversely, the negative Raman bands show features that diminish upon deprotonation of this polymer. For the reduced form, two very intense negative Raman bands are observed (Fig. 2). These relate to very characteristic features of leucoemeraldine, C–C band

stretching vibrations in benzene rings around 1623 cm^{−1} and C–H bending vibrations around 1186 cm^{−1}. Also, two weak or mid-intense negative bands centered around 883 cm^{−1} and 830 cm^{−1}, representing benzene ring deformations, are well seen (Fig. 2). Thus, a decrease in the intensity of all Raman bands for a leucoemeraldine form upon deprotonation is observed at the blue laser line excitation. For the oxidized form, both positive and negative difference bands are observed (Fig. 2). Among them, again, mid-intense or strong negative bands around 1622 cm^{−1} and 1194 cm^{−1} appear dominating over the entire difference spectrum. As compared to the reduced form, the frequency of the latter band for the oxidized form appears upshifted by 8 cm^{−1}. Also, same as to reduced form, two weak or mid-intense negative differ-

ence bands at 884 cm^{−1} and 830 cm^{−1} are well seen. In addition to the negative bands, a set of weak or mid-intense positive difference bands are observed. All these bands could be tentatively ascribed to the features of the oxidized form. These are: a weak positive band at 1594 cm^{−1} that could be assigned to the C=C stretching in quinone type rings, a mid-intense band at 1455 cm^{−1}, corresponding to the C=N stretching (imine sites), and a mid-intense band at 1167 cm^{−1}, corresponding to the C–H bending in emeraldine or pernigraniline in their deprotonated forms. The tentative assignments for the most prominent difference Raman bands observed are summarized in Table.

The green laser line excitation at 532 nm results in a rich set of positive and negative difference Raman bands, both for reduced and oxidized forms of

Table. **Tentative assignments of difference Raman bands (cm^{−1}) as obtained for different spectra excitation wavelengths**

Difference bands (pH 9 minus pH 1) at selected excitation wavelengths								Tentative assignments
442 nm		532 nm		633 nm		785 nm		
Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized	
1623 ↓(s)	1622 ↓(s)	1628 ↓(s)						C–C stretching in B (8a)
		1614 ↑(m)	1613 ↑(m)	1614 ↑(s)	1612 ↑(m)	1610 ↑(m)	1605 ↑(m)	
	1594 ↑(w)	1589 ↑(m)	1594 ↑(s)	1591 ↑(s)	1594 ↑(s)			C=C stretching in Q (8a)
		1530 ↑(m)	1530 ↑(s)		1542 ↑(m)			
		1500 ↑(w)						
	1455 ↑(m)	1441 ↑(m)	1450 ↑(vs)	1458 ↑(vs)	1460 ↑(vs)	1444 ↑(s)	1452 ↑(vs)	C=N stretching in emeraldine base (imine sites)
		1419 ↑(s)	1427 ↑(sh)	1423 ↑(sh)	1427 ↑(sh)	1419 ↑(s)	1424 ↑(s)	
		1380 ↑(sh)						C~N[+] stretching in polaronic form (polarons)
		1341 ↓(w)		1344 ↓(m)				
		1316 ↓(w)		1320 ↓(m)				
		1221 ↑(m)	1221 ↑(s)	1221 ↑(m)	1221 ↑(s)	1222 ↑(m)	1222 ↑(s)	C–N stretching in emeraldine (amine sites)
1186 ↓(s)	1194 ↓(s)	1189 ↓(s)				1180 ↑(w)		C–H bending in leucoemeraldine (9a)
	1167 ↑(m)	1161 ↑(s)	1161 ↑(s)	1161 ↑(s)	1161 ↑(s)	1159 ↑(m)	1163 ↑(vs)	C–H bending in emeraldine (9a)
		1048 ↓(w)	1051 ↓(w)					
		980 ↓(w)	978 ↓(w)					
883 ↓(w)	884 ↓(w)	886 ↓(w)	883 ↓(w)					
			847 ↓(w)		847 ↑(m)	841 ↑(w)	844 ↑(m)	B deformation (1)
830 ↓(m)	830 ↓(m)	833 ↓(m)						
		777 ↑(m)	777 ↑(m)	782 ↑(m)	780 ↑(m)	780 ↑(w)	781 ↑(m)	Q deformation

Table. (Continued)

Difference bands (pH 9 minus pH 1) at selected excitation wavelengths								Tentative assignments
442 nm		532 nm		633 nm		785 nm		
Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized	Reduced	Oxidized	
			747 ↑(m)	747 ↑(w)	750 ↑(w)	745 ↑(w)	747 ↑(m)	Imine deformation (C–N–C bending)
			588 ↓(w)		589 ↓(w)			
		530 ↑(m)	530 ↑(m)	528 ↑(m)	530 ↑(m)	528 ↑(m)	528 ↑(m)	Amine in-plane deformation
		429 ↑(m)	421 ↑(m)					
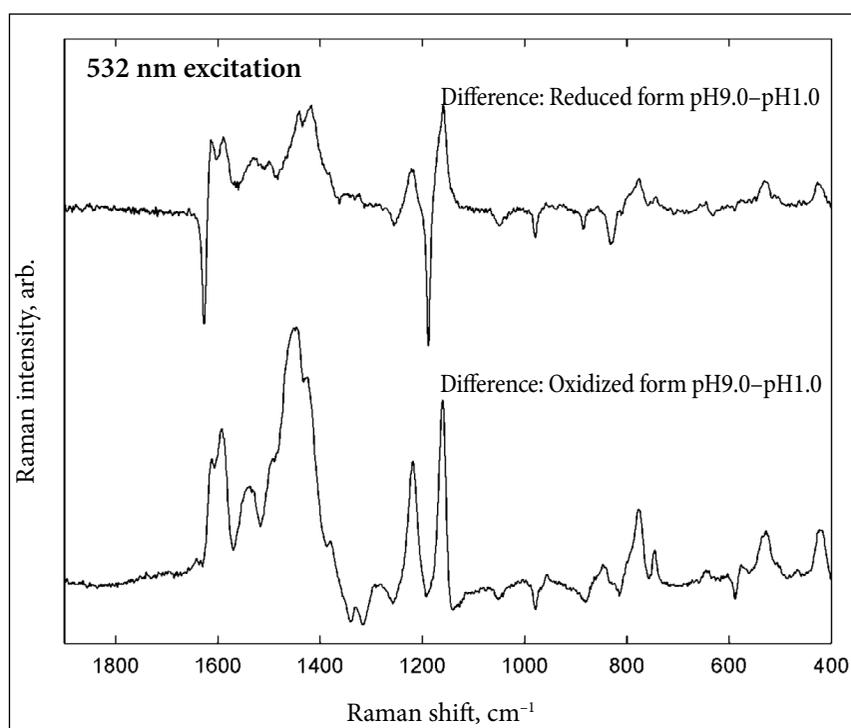
Fig. 3. Same as in Fig. 1, as obtained at 532 nm laser line excitation

polyaniline (Fig. 3). As we discussed in our previous papers [8–11], the main difference between these two excitation wavelengths is in different resonance of laser lines with the differently coloured forms of polyaniline. A blue laser line appears in a partial resonance with the leucoemeraldine form, whereas both reduced and oxidized forms are well distinguishable with the green line excitation. Similarly as with the blue excitation, two very characteristic strong negative bands are observed upon deprotonation for the reduced form located at 1628 cm^{-1} and 1189 cm^{-1}, corresponding to the C–C stretching in benzene rings, and C–H bending vibrations, respectively (Table). Similarly, two less expressed negative difference

bands of benzene ring deformations at 886 cm^{-1} and 833 cm^{-1} are observed as well.

Assignments are based mainly on the known data [1–6, 8–10]. Difference spectra were obtained by subtracting the spectra obtained at solution pH 1 from those obtained at solution pH 9 separately for reduced and oxidized forms. The arrows (↓) and (↑) indicate the tendencies for a decrease or an increase of intensity for spectral bands, respectively, the symbols (1), (8a) and (9a) denote Wilson's notations of vibrational modes for benzene derivatives.

Next to these, a number of positive difference bands are present in spectra (Fig. 3). Among them, a definite group of positive difference bands deserve a separate consideration. Within this group,

a mid-intense band at 1589 cm^{-1} corresponds most probably to the C=C stretching vibration in quinone type rings, and thus is a feature for the oxidized form of polyaniline. In its oxidized form, this band appears at 1594 cm^{-1} as a strong positive band. Again, a mid-intense band at 1441 cm^{-1} is observed, belonging very probably to the C=N stretching vibration in the partially oxidized form. For the oxidized form, the corresponding positive band appears at 1450 cm^{-1} as a very strong positive band dominating over the entire spectrum (Fig. 3). Next to the strong negative band at 1189 cm^{-1} discussed above, a strong positive difference band around 1161 cm^{-1} is observed both in reduced and oxidized forms, corresponding to the C–H bending vibration in an emeraldine form. Similarly, in addition to the negative benzene ring deformations at 886 cm^{-1} and 833 cm^{-1} mentioned above as characteristic features for the reduced form, a positive mid-intense band at 777 cm^{-1} appears, probably corresponding to quinone ring deformations and therefore present in the spectrum for the oxidized form as well. These observations show that even the electrochemically reduced form of polyaniline shows some features of the oxidized form. Admittedly, same features appear more intensive expressed in the spectra of the electrochemically oxidized form. Most probably, the features of the oxidized form are observed for the reduced form at the expense of some

amount of the oxidized form present within the layer of the reduced form. This presence appears very probable owing to the incomplete electrochemical oxidation or reduction processes. This incompleteness is a well-known issue that causes some specific phenomenon like, e.g. a 'first cycle effect' or slow relaxation phenomenon [13].

The results obtained show that the intensity of Raman features for the reduced form of polyaniline diminishes upon deprotonation both with the use of the blue and green laser line excitation, since intense negative difference Raman bands are observed. In contrast, a general growth of band intensity upon deprotonation occurs for the characteristic features of the oxidized form at a green laser line excitation, even for a supposedly small amount of this form present within the bulk of the reduced polymer layer, as it could be deduced from the presence of a lot of positive difference Raman bands (Table).

In contrast to blue and green line excited spectra, the situation changes drastically at a red laser line excitation of 633 nm (Fig. 4). As discussed previously [9, 10], the red line falls into a resonance with a blue coloured oxidized form, thus, almost no features of the reduced form are observed. With the red line excitation, the reduced form shows a number of positive difference Raman bands (Fig. 4). Despite of some variations, all these difference bands
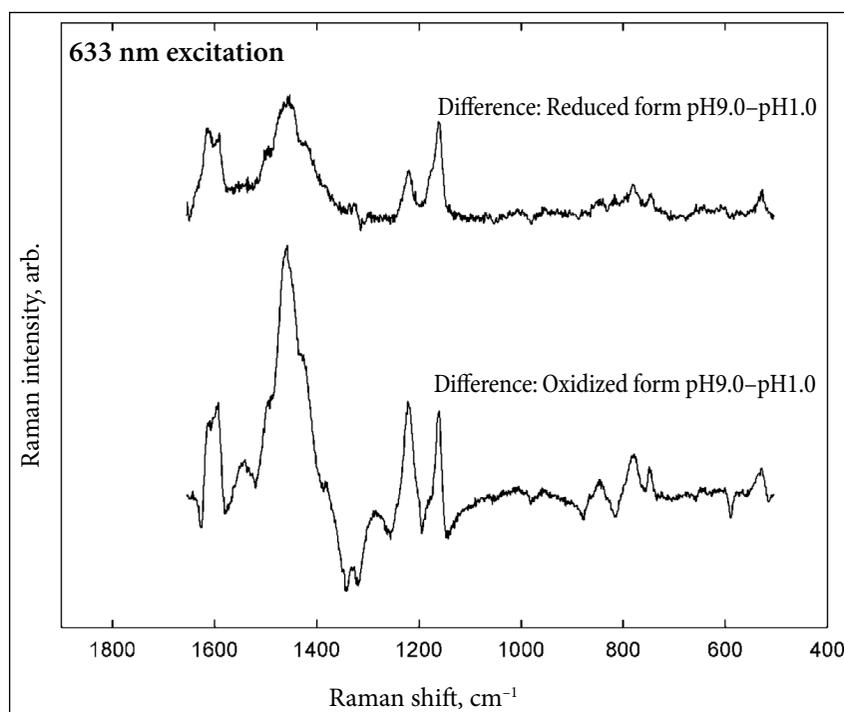
Fig. 4. Same as in Fig. 1, as obtained at 633 nm laser line excitation

arise very probably from the oxidized form, present in a small amount in the modifier layer at the electrode. The table presents a comparison for these bands. The main bands are as follows. A strong difference band at 1594 cm^{-1} belongs to the C=C stretching vibration in quinone rings. A closely similar band is observed for the oxidized form (Table). Noteworthy, there is no band around 1620 cm^{-1}, as it could be expected for reduced species as a characteristic feature for benzene rings. Again, very strong difference bands at 1458 cm^{-1} or 1460 cm^{-1} appear dominating over the entire difference spectrum for reduced and oxidized forms, respectively (Fig. 4), representing the C=N stretching vibration in the oxidized form. This difference Raman band appears probably as most indicative and depending on the spectra excitation wavelength used. At the 442 nm excitation, this band appears mid-intense only for the oxidized form, at the 532 nm excitation, its moderate intensity for the reduced form changes to very strong upon electrooxidation, whereas a very high intensity is characteristic for both these redox forms at the 633 nm excitation (Table). As the next difference bands characteristic for both redox forms, a strong band at 1161 cm^{-1}, representing the C–H bending mode in emeraldine, and a mid-intense band at 782–780 cm^{-1} should be mentioned (Table). The analysis of difference Raman bands for the reduced form at the 633 nm exci-

tation (Fig. 4) shows that i) most probably, only characteristic features for the oxidized form, presumably present in a small quantity in a bulk of reduced form, are observed, and ii) the entire intensity of difference spectra grows highly upon deprotonation.

In addition to positive difference bands, the red excitation yields for the oxidized form of polyaniline some negative bands as well (Fig. 4). From these, two bands located around 1344 cm^{-1} and 1320 cm^{-1} should be mentioned. Noteworthy, the reduced form does not show any analogous bands within this spectral range. A very similar situation was observed for the green excitation, where the same two bands were observed for the oxidized form, followed by absence of them for the reduced form (Table). Most probably, these two bands belong to a polaronic form of polyaniline, containing an intermediate between a single and a double C~N band order. We discussed the presence of these two kinds of polarons [14]. In conclusion, a high increase of an overall intensity of the Raman spectrum at this red excitation should be noted for the electrochemically oxidized form of polyaniline.

A far red, or near infrared, excitation at 785 nm, again, falls into a resonance with the red absorbing oxidized form of polyaniline, therefore, specific features for this form, resembling those observed with the 633 nm excitation, are recorded (Fig. 5).
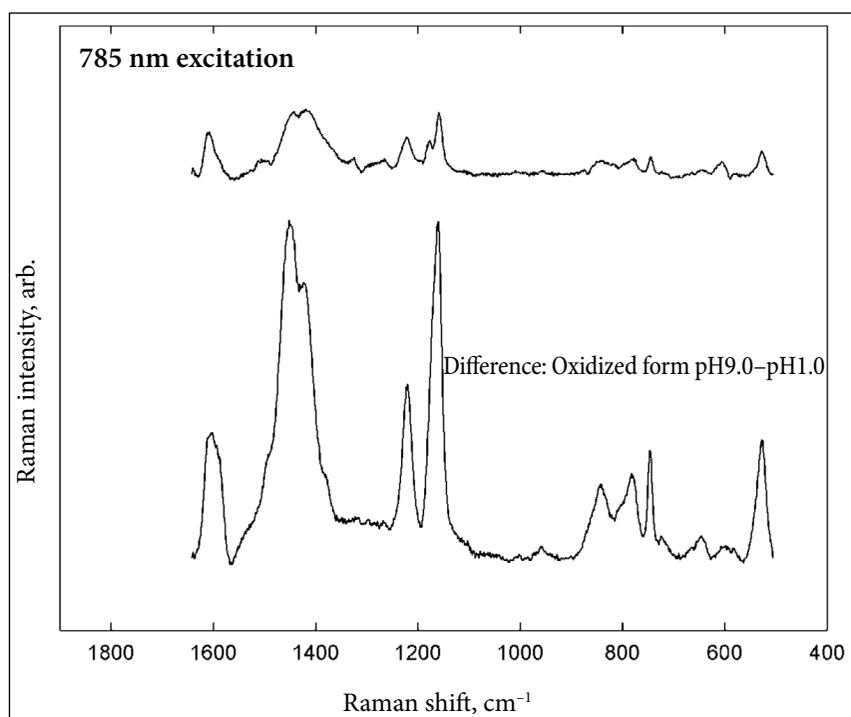
Fig. 5. Same as in Fig. 1, as obtained at 785 nm laser line excitation

Similarly, the C=N stretching vibration (imine sites) appears as strong or very strong difference bands both for reduced and oxidized forms at 1444 cm^{-1} and 1452 cm^{-1}, respectively, whereas the C–N stretching vibration (amine sites) develops around 1222 cm^{-1} as mid-intense or strong difference bands for both redox forms (Table). Also, mid-intense (for the reduced form) or very strong (for the oxidized one) difference bands located around 1159 cm and 1163 cm^{-1}, respectively, are present as a characteristic of C–H bending vibrations. Noteworthy, no negative difference bands within a range of approximately 1350–1300 cm^{-1} were observed, as it could be expected for polaronic species, well observable at the 633 nm excitation. From the difference spectra obtained at the 785 nm excitation, it could be concluded that, because of a resonance enhancement, only specific features of the oxidized form of polyaniline are observed. As with the reduced form, the spectra obtained should originate from a small amount of the oxidized form, present within the bulk of a polymer film at the electrode surface. Also, it is seen from Fig. 5 that deprotonation leads to a drastic increase of intensity, especially for the oxidized form. In this respect, this behaviour resembles that observed at the 633 nm excitation.

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Regina Mažeikienė, Gediminas Niaura, Albertas Malinauskas

POLIANILINO DEPROTONAVIMO PROCESŲ TYRIMAS ELEKTROCHEMINĖJE SISTEMOJE NAUDOJANT SKIRTUMINĘ DAUGIABANGĘ RAMANO SPEKTROSKOPIJĄ

S a n t r a u k a
Polianilino sluoksnis buvo nusodintas ant aukso elektrodo ir tirtas panaudojant skirtuminę daugiabangę Ramano spektroskopiją. Spektrams sužadinti naudotos kelių skirtingų bangų ilgių lazerių linijos: mėlyna (442 nm), žalia (532 nm), raudona (633 nm) ir tolima raudona (785 nm). Remiantis gautais rezultatais, sudaryti ir išanalizuoti skirtuminiai Ramano spektrai tarp deprotonuotos (esant pH 9,0) ir protonuotos (esant pH 1,0), oksiduotos ir redukuotos polianilino formų. Identifikuotos būdingosios skirtingų polianilino formų ypatybės ir parodyta šių ypatybių priklausomybė nuo spektrų sužadinimo bangos ilgio. Skirtuminė Ramano spektroskopija sudaro sąlygas tirti dėl grįžtamųjų protonavimo procesų pasirinktų Ramano spektrinių linijų intensyvumo kitimą.