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In situ Raman spectroelectrochemical study of electrocatalytic processes at polyaniline modified electrodes: Redox vs. metal-like catalysis

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Abstract

Two processes of electrocatalytic oxidation of solution species at conducting polymer modified electrodes have been studied for the first time with in situ Resonance Raman spectroelectrochemical technique at a red laser excitation ($\lambda = 632.8$ nm), namely electrooxidation of hydroquinone at a sulfonated polyaniline modified electrode in an acidic solution and electrooxidation of ascorbic acid at polyaniline modified electrode in a pH-neutral solution. In both cases, characteristic Raman features have been identified for different redox forms of conducting polymers and changes in the net redox state of a polymer layer during electrooxidation of solution species have been studied. It has been shown that an increase in the concentration of oxidizable species causes an increase of the net content of a reduced form of polyaniline in the modifying layer. From this, the redox (vs. metal-like) mechanism of electrocatalysis at conducting polymer modified electrodes has been deduced.

Keywords: Polyaniline; Electrocatalysis; Ascorbic acid; Hydroquinone; Raman spectroelectrochemistry; Modified electrodes

1. Introduction

Electrocatalytic conversion of solute species at conducting polymer modified electrodes presents a fast growing research field due to numerous possible applications of this phenomenon both in electrosynthesis and electroanalysis [1]. One of the most important problems related to electrocatalysis at conducting polymers is the location of electrocatalytic site. At indefinitely great mobility of charge carriers (i.e., electrons and holes) within the electrode material, the electrocatalytic redox reaction takes place at the outer electrode/solution interface, resembling the behavior of a metallic electrode. The electric conductivity of the most conducting polymers like polyaniline is of a semiconductor type rather than metallic. Therefore, because of a limited mobility of charge carriers within a conducting polymer film, the electrocatalytic redox reaction should take place within the porous polymer film rather than at an outer polymer/electrolyte interface. The depth of this virtual reaction layer should depend mainly on the balance between the fluxes of reactant species from the solution and of charge carriers through the polymer layer.

In an electrochemical study on electrocatalytic reduction of benzoquinone at polyaniline modified electrode, Cooper and Hall [2] claimed the occurrence of this reaction at polymer/electrolyte interface in an acidic solution, whereas, at a higher pH, charge transfer through the polymer appears to be slow and no reduction of benzoquinone occurs on the outside, instead occurring in a layer at the electrode. In a detailed rotating disc electrode study, Bartlett et al. [3] found that electrocatalytic oxidation of coenzyme NAD(P)H at a

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glassy carbon electrode, modified with polyaniline–polyvinylsulfonate composite, occurs within the film rather than just at the outside. Mandic and Duic [4] presented evidences on metal-like behavior of polyaniline at potentials of its emeraldine (half-oxidized) form (i.e., occurence of redox reactions at the polymer/solution interface), and on redox-polymer behavior at potentials of pernigraniline (fully oxidized) form (i.e., electrocatalytic conversion within the polymer film) for hydroquinone/benzoquinone and $Fe^{2+/3+}$ redox couples.

Scarce and indirect information on the reaction site for electrocatalytic conversions of solute species at conducting polymer modified electrodes, supplied by electrochemical techniques, could be beneficially complemented by the use of direct in situ spectroelectrochemical techniques. Electrocatalytic oxidation of hydroquinone and reduction of benzoquinone, Fe^{3+} ions, and 1,2-naphthoquinone-4-sulfonate has been found to occur within polyaniline layer, as studied with in situ UV–Vis spectroelectrochemical technique at polyaniline-modified ITO glass electrodes [5,6]. Same mechanism of electrocatalytic oxidation of hydroquinone and reduction of benzoquinone has been claimed based on UV–Vis spectroelectrochemical study for a layer of poly(*N*-benzylaniline) [7].

Next to UV–Vis spectrovoltammetry, other direct in situ techniques seem to be very desirable for the study of electrocatalytic reactions at conducting polymer modified electrodes. In the present event, we report the use of a resonant Raman spectroscopy (RRS) for in situ study of electrocatalytic oxidation of hydroquinone and ascorbic acid at electrodes, modified with polyaniline and its sulfonated derivative. On our knowledge, this is the first study on in situ application of RRS to electrocatalytic conversions of solute species at conducting polymer modified electrodes.

2. Experimental

Aniline has been distilled before use. *m*-Aminobenzenesulfonic acid (metanilic acid) and other chemicals were of analytical or reagent grade, and have been used as received.

Raman spectroelectrochemical experiments have been performed in a closed cylindrical three electrode cell. A circular gold electrode of ca. 5 mm in diameter, press-fitted into a Teflon rod, was used as a working electrode. Platinum wire and a saturated Ag/AgCl electrode were used as a counter and reference electrodes, respectively. All potential values reported refer to saturated Ag/AgCl electrode. The working electrode was placed at ≈5-mm distance from the cell window and a He–Ne gas laser (Spectra Physics, Inc.) beam at $\lambda = 632.8$ nm with the power restricted to 10 mW was incident on the surface at ≈60° and focused to a spot of ≈1 mm^2 in area. The experiments were performed in 90° geometry. The laser plasma lines were attenuated by means of an interference filter. The Raman scattering light was analyzed by *f*/2.5 custom built spectrometer equipped with 600 lines/mm grating and detected by the thermoelectrically cooled (−40 °C) CCD detector (Model ST-6, Santa Barbara Instrumental Group, Inc.). The cut-off filter was put in front of the spectrograph to eliminate Rayleigh scattering from the electrode.

PI-50-1 model potentiostat, arranged with PR-8 model programmer, was used throughout the experiments. Before each experimental set, the gold working electrode has been cleaned for 1 h in a Piranha solution (a mixture of 30% hydrogen peroxide solution and concentrated sulfuric acid, 3:1 by vol.). Electrosynthesis of a copolymer of aniline and metanilic acid has been performed by applying of a controlled potential of 0.8 V for 30 min in a solution of 0.1 M of sulfuric acid containing 0.1 M of metanilic acid and 0.01 M of aniline. Electrosynthesis of polyaniline has been done in a similar manner in a solution containing 0.1 M of sulfuric acid and 0.01 M of aniline.

3. Results and discussion

3.1. Electrooxidation of hydroquinone at sulfonated polyaniline electrode

Sulfonated polyaniline (SPAN) presents a copolymer of aniline and its sulfonated derivative, *m*-aminobenzenesulfonic acid (metanilic acid), obtained by electropolymerization procedure. As distinct from polyaniline (PANI), SPAN shows a narrower potential window for the existence of its conducting emeraldine form, ranging from ca. 0.24 V (i.e., the midpoint potential for leucoemeraldine to emeraldine redox transition) to ca. 0.41 V (the midpoint potential for emeraldine to pernigraniline transition) in 0.1 M sulfuric acid solution, used in the present work [8]. The redox capacity of SPAN modified electrode prepared varies as usual between 10 and 15 mC/cm^2, as obtained by potential scan between −0.1 and 0.8 V.

At a controlled potential of 0.6 V, where a fully oxidized form – pernigraniline – prevails, the red laser excitation ($\lambda_{ex} = 632.8$ nm) yields the resonance Raman spectrum, typical for polyanilines (Fig. 1). The Raman bands observed could be ascribed to definite vibrations based on known assignments [9–15]. A strong band at 1180 cm^{-1} can be attributed to bending C–H vibration mode of quinoid-like rings $\delta(CH)_Q$ (9a mode according to Wilson's notation). Two overlapping bands within the range of 1300–1400 cm^{-1}, centered at 1337 and 1363 cm^{-1} belong most probably to polarons, i.e. to stretch vibrations of a $C–N^+$ molecular fragment having