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Evaluation of the electrochromic response of polypyrrole in the presence of CO_2 in the solution

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Abstract:

The indium tin oxide (ITO) coated glass was used as a working electrode for electrochemical deposition of conducting polymer polypyrrole (Ppy). Before polymerization, the electrode surface was additionally modified with triethoxymethylsilane (TEMS) to provide better adhesion of polypyrrole to the surface of ITO [1]. Polymerization of Ppy was performed electrochemically regarding the previous studies [2, 3, 4]. The ionic strength of the solution was supported by $LiClO_4$.

Since the dissolved CO_2 in the solution forms the weak acid and thus the pH of a solution can be slightly changed the electrochromic response to the pH changes was evaluated. Britton – Robinson buffer (BRB) was used as the model system for evaluation of the electrochromic response of polypyrrole at different pH values and concentrations of $NaHCO_3$, which was a source of CO_2 in the solution.

For the evaluation of electrochromic response in the presence of CO_2 the double potential step chronoamperometry method was applied and UV-Vis absorption spectra were registered. To gain insight into the charge transfer phenomenon in more detail, the cyclic voltammetry experiments at different glass/$ITO_{(TEMS)}$/Ppy electrode potential sweep rates were performed.

Keywords: conductive polymer; polypyrrole (Ppy); electrochemical polymerization; electrochromic properties.

Experimental:

Materials and methods:

All the chemicals were of analytical grade and were used as obtained except pyrrole, which distilled before the use.

Britton – Robinson buffer (BRB): 0.01 M boric acid, 0.01 M acetic acid, 0.01 M phosphoric acid, and 0.1 M $LiClO_4$. The pH of BRB was adjusted with 1.0 M NaOH.

Pretreatment of indium tin oxide coated glass electrode (ITO):

15–25 Ω/sq was purchased from Sigma-Aldrich (Steinheim, Germany) was cleaned in several steps: 1) ultra-pure water; 2) 27% NH_4OH and 30% H_2O_2 mixed at ratio 3:1 and preheated up to 50°C for the 5 min; 3) water for 15 min; 4) acetone for 15 min; 5) water for 15 min.

Modification of ITO:

The glass/ITO surface was modified with 4% (v/v) solution of triethoxymethylsilane (TEMS) in acetone overnight and correspondingly TEMS modified structure (glass/ITO(TEMS)) was formed. After modification, ITO was washed with acetone and ultra-pure water.

Electrochemical deposition of polypyrrole (Ppy) on ITO:

A computer-controlled potentiostat/galvanostat PGSTAT 128N with Nova 1.10 software from Eco-Chemie (Utrecht, The Netherlands) was used electrochemical measurements. Pyrrole was polymerized electrochemically from a solution containing 10 mM of pyrrole and 0.1 M of $LiClO_4$.

Three electrode system consisted of:

RE – $Ag/AgCl_{(3M\ KCl)}$, CE – platinum wire, and WE – glass/ITO/Ppy.

Evaluation:

The absorbance was measured with a spectrometer USB4000-FL with 'SpectraSuite' software (Ocean Optics, Largo, USA).

Absorbance spectra were registered during a potential alternation from −0.9 V to +0.2 V in the BRB solution, pH 2.3 and pH 7.

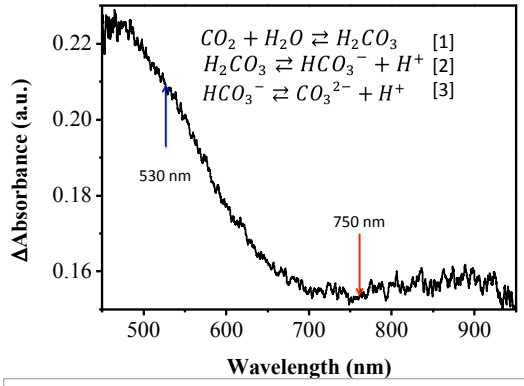

Fig. 1. The UV-vis absorbance spectra of glass/ITO/Ppy.

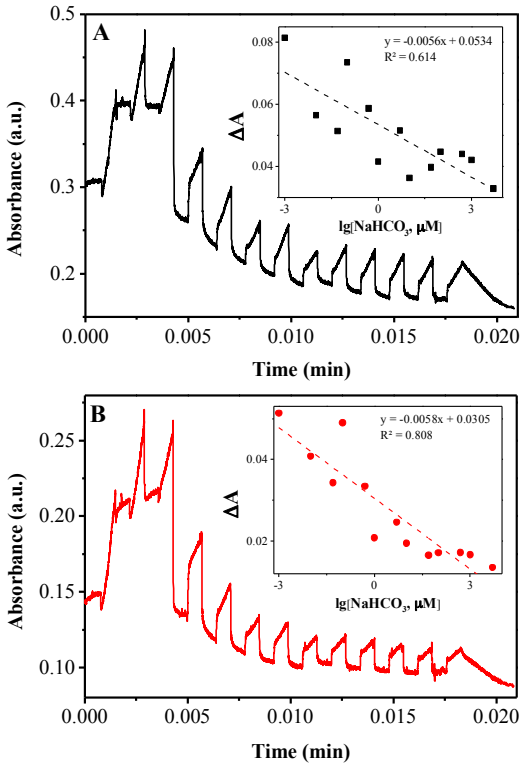

Fig. 2. Absorbance at wavelengths of (A) 530 nm and (B) 750 nm *vs.* time profile obtained during a potential alternation from −0.9 V to +0.2 V vs $Ag/AgCl_{(3M\ KCl)}$ in the BRB solution, pH 2.3.

The inserts: The dependence of ΔA at 530 nm and 750 nm wavelengths on the concentration of $NaHCO_3$. ΔA=ΔAbsorbance = $Absorbance_{-0.9\ V}$ – $Absorbance_{+0.2\ V}$.

Conclusions:

It was demonstrated, that there is dependence of absorbance at 750 nm wavelength on the concentration of $NaHCO_3$ in the BRB solution only if pH is acidic, i.e. pH 2.2. There wasn't observed any dependence of absorbance, neither in more alkaline BRB solutions, either at 530 nm wavelength.

But the dependence of ΔAbsorbance at 530 nm and 750 nm wavelengths on the concentration of $NaHCO_3$ in the BRB solution, pH 2.3 was observed, when a potential was alternated from −0.9 V to +0.2 V *vs.* $Ag/AgCl_{(3M\ KCl)}$.

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