

# Analysis of high-frequency distortions in impedance spectra of conducting polyaniline film modified Pt-electrode measured with different cell configurations

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## Abstract

Distortions of high-frequency parts of impedance spectra of conducting polyaniline, PANI, film modified Pt electrodes in 0.5 and 0.05 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> are analysed in terms of overlapping between impedance of PANI film working electrode (WE) branch and artefact impedance(s) induced by measurements in two-electrode (symmetrical, PANI versus PANI and asymmetrical, PANI versus platinised Pt) and three-electrode (with conventional reference (RE) and pseudo-reference (PRE) electrode) cells. In impedance measurements with both two-electrode cell configurations and PANI film WE at equilibrium, high-frequency distortions are generated by contribution of inductive impedance originating from instruments and wirings. Extent of distortions is found inversely proportional to the solution resistance term. In impedance measurements with conventional three-electrode cell configuration and PANI film WE kept at polarized conditions, relatively high extent of high-frequency distortions is generated by couplings between three electrodes of similar impedances. Distortions are manifested as inductive/capacitive artefact impedance, with lower inductivity and higher capacity for lower solution resistance and *vice versa*. Low impedance PRE is found useful for simultaneous diminishing of inductive and capacitive artefact impedances, what in some conditions could result with impedance spectra showing minor high-frequency distortions. Use of proper transfer function(s) with impedance of experimental artefacts involved, is in all cases found essential not only for determination of all parameters characterizing fast impedance response of PANI film WE, but for highlighting physical origins and possible ways of control of the content of experimental artefacts in measured impedance spectra too.

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## 1. Introduction

Higher or lower extent of overlapping between impedance of the working electrode (WE) impedance branch and some additional impedance(s) causing distortions of high frequency parts of impedance spectra measured with conventional three-electrode cell and liquid electrolytes, has already been stressed as a general problem of electrochemical impedance spectroscopy technique [1–6]. Overlapping between various impedance responses was found particularly evident in measurements of either highly resistive WE branch (electrode and solution of low

conductivity) [3,4,7,8], or highly conductive WE branch (electrode and solution of high conductivity) [9–13]. In both cases, distortions originating not only from reference (RE) and counter (CE) electrodes and their geometrical arrangement [3,4,7,8,13], but also from measuring instrumentation and wirings [9–11], have been recognized as main sources of additional impedances termed as experimental artefacts. Although impedance measurements in two-electrode configuration are generally free from experimental artefacts caused by electrical couplings between electrodes [1,5,6,14], some contributions from stray capacities and inductivities were found pronounced in measurements of (very) high and (very) low impedance cells, respectively [6,14,15]. These parasitic impedances were considered to be generated by instrumentation, wirings and physical body of the cell, i.e. material(s), overall design (geometry) and environment of the cell. In already presented impedance spectra of low impedance and highly capacitive WE such as conducting form of

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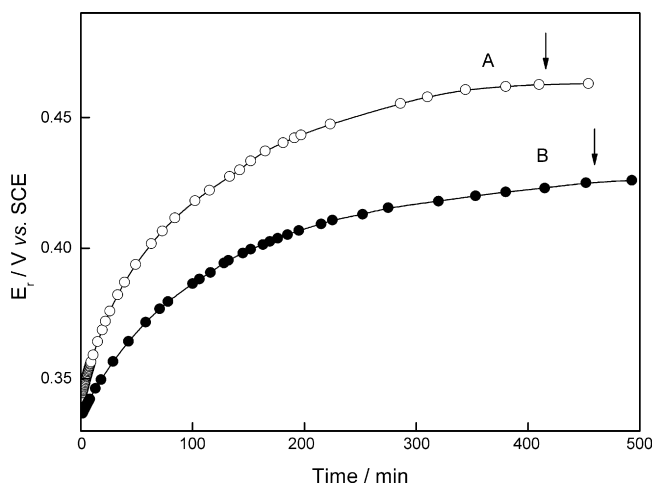


Fig. 1. Time dependence of  $E_t$  during equilibration of conducting PANI modified Pt electrode in: (A)  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  and (B)  $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Time of starting impedance measurements is denoted by arrows.

polyaniline (PANI) film modified electrodes and/or PANI membranes in acidic solutions, relatively high extent of distortions could be noticed in high frequency parts of impedance spectra measured in either conventional three-electrode cell [16–18], in three-electrode cell with RE connected with pseudo-reference electrode (PRE) [9,10,12,13], or in four-electrode cell with

two RE's [17,19]. Since in the case of highly capacitive and low impedance WE, presence of parasitic impedances and/or reflections of RE and CE in measured impedance spectra could hardly be avoided, even after using PRE placed close to RE [9,10,12,13], it seems to be of high importance to distinguish and separate their frequency response from the frequency response of impedance branch containing conducting PANI film WE. Characterization, distinguishing and separation of overlapping impedances at high frequencies might be relevant not only for recognition and characterization of all processes influencing short-time response of conducting PANI films what is important for a number of conducting PANI films applications [20], but for definition of physical origins and possible control of the content of experimental artefacts in impedance measurements too.

## 2. Experimental

PANI modified Pt electrodes have been prepared by  $50 \text{ mV s}^{-1}$  potential cycling of Pt wires (0.09 and  $0.18 \text{ cm}^2$  in superficial area) from the solution containing  $0.1 \text{ mol dm}^{-3}$  aniline and  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ , until pre-determined thicknesses ( $\sim 500 \text{ nm}$ ) were attained [12,21]. After the first potential scan was passed, the potential range of scanning between  $-0.20$  and  $+1.05 \text{ V}$  versus SCE is diminished to  $-0.20$  and  $+0.85 \text{ V}$

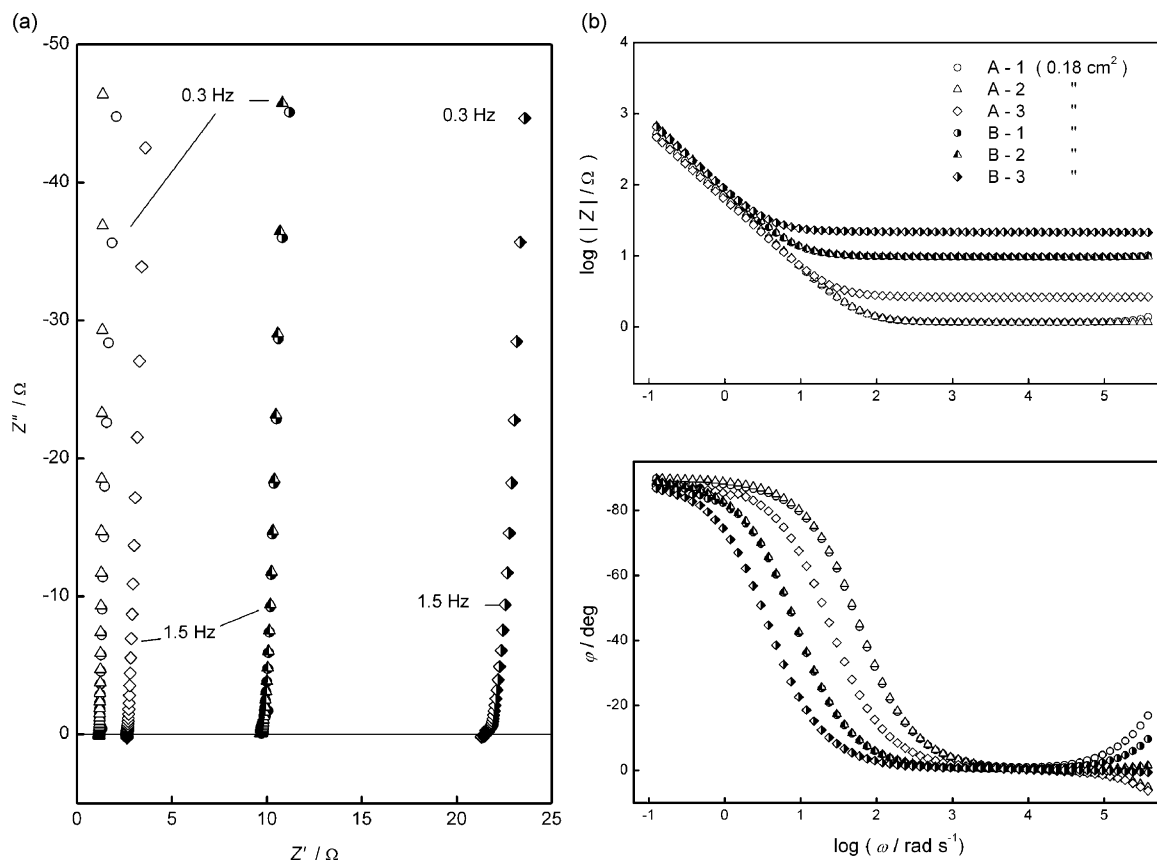


Fig. 2. Experimental (a) complex impedance and (b) Bode plots of conducting PANI film modified Pt electrode ( $0.18 \text{ cm}^2$ ) in (A)  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  and (B)  $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  measured at  $+0.35 \text{ V}$  vs. SCE in (1) three-electrode cell with conventional RE, (2) three-electrode cell with RE/PRE configuration,  $C_c = 1 \times 10^{-6} \text{ F}$  and (3) at equilibrium in asymmetric, PANI vs. platinumised-Pt, two-electrode cell.

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