# The Explanation of Negative Capacitance for Polyaniline via Electrochemical Impedance Spectra

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## Introduction

Conducting polymers have been widely studied in the last two decades, especially with an aim to find suitable applications. The potential uses of conducting polymers as materials in rechargeable batteries, electromagnetic interference shielding, sensors, and electrochromic display devices have been well establisthed. Among all the conducting polymers, polyaniline (PANI) is particularly an attractive material owing to its good electrical, optical and electrochemical properties as well as good environmental stability. From earlier publications [1-4], PANI under the higher oxidized state was reported to be gradually converted to the degradation products such as benzoquinone (BQ) due to hydrolysis. It is anticipated that the presence of certain amount of BQ/HQ in PANI may provide a novel utilization of PANI to provide inductive behavior (negative capacitance) in electric circuits. Consequently, the behavior of BQ/HQ in PANI film is worth for further investigating for negative capacitance, which in turn will be useful to understand the interactions of BQ/HQ during the redox transitions in PANI. Electrochemical impedance spectroscopy (EIS) is a handy tool to test the inductive loop of BQ/HQ in PANI films.

## Results and Discussion

Two different Polyaniline films were deposited by using cyclic voltammetry. For one type of PANI film (denoted as film-a) potential was swept between –0.15 and 0.90 V. For the other film (denoted as film-b) potential range of –0.15 to 0.75 V was used.

An interesting phenomenon can be noticed from the impedance spectrum in Fig. 1, i.e., the impedance responses of PANI film-a at 0.7 V. Meanwhile, a decrease in the real part and an increase in the imaginary part are simultaneously observed in the low-frequency region. This impedance response in the low-frequency region reveals the inductive loop.

Since the redox transition corresponding to the benzoquinone/hydroquinone (BQ/HQ) redox pair occurs between 0.5 and 0.7 V, the presence of the inductive loop in this potential range is probably explained by the significant contribution of the BQ/HQ transition. The protons which are expelled when PANI in the emeraldine form oxidizes to the nigraniline form, converts BQ to HQ. In the reverse process, the reduction of PANI in nigraniline form to the emeraldine form requires the addition of protons to complete the process, which can be considered to be donated from HQ, favoring the oxidation of HQ and loss of protons to form BQ. Hence, the negative capacitance of the polymer is found within this potential range. Since inductive loop results from the electrochemical oxidation/reduction of the BQ/HQ pair, this inductor is defined as an electrochemical inductor.

To verify the hypothesis of negative capacitance by the presence of significant amount of BQ/HQ redox pair within the PANI film, the EIS data of PANI film-b polymerized with an upper potential limit of 0.75 V were also subjected. Typical impedance spectra measured at 0.7 V are shown in Fig. 2. The use of less positive upper potential limit for the polymerization to deposit film-b makes low proportion of BQ/HQ pairs within PANI film. This renders the disappearance of the inductive loop in the low-frequency region on the spectra in Fig. 2. Consequently, the presence of significant amount of BQ/HQ redox pair within the PANI film is identified as the reason for the electrochemical negative capacitance in the low-frequency region.

## References

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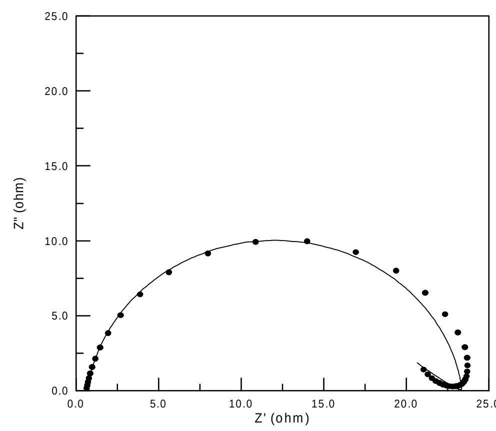


Fig. 1. Nyquist diagram for PANI film-a measured at 0.7V. The solid line represents the best fitting results according to the equivalent circuit.

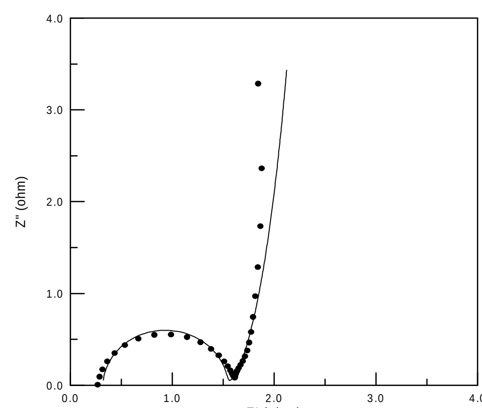


Fig. 2. Nyquist diagram for PANI film-b measured at 0.7V. The solid lines represents the best fitting results according to the equivalent circuit.