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# Electro-oxidation of polyaniline in the presence of electronic acceptors and the magnetic properties of the resulting polyaniline

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## ABSTRACT

Reduced polyaniline (PANI) exhibits a Nernstian response to dissolved electronic acceptors chloranil (CHR) with a linear relationship between electrode potential and the logarithm of the concentration of the acceptors ( $\log C$ ) with the positive slope. On the other hand, in the cyclic voltammograms showing the redox activities of PANI on the electrode surface, the peak potential is proportional to  $\log C$  with the negative slope. These linear relationships imply an electronic interaction between PANI and the acceptors. The comparison of the PANIs before and after the contact to the acceptors in the UV–visible absorption spectra and elemental composition revealed that the interaction not only transforms the electronic state of PANI, but also incorporates the acceptors. Both measurements of electron spin resonance (ESR) and magnetic susceptibility demonstrate that the incorporation magnetized PANI. Although the PANI incorporating CHR shows no ferromagnetism, it possesses paramagnetic properties, which do not obey the Curie–Weiss law. In addition, further analysis of the ESR spectra reveals that the radical species are stabilized in the polymer chains.

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## 1. Introduction

Conductive polymers possess useful properties applicable to electronic devices such as electrochromic displays, electronic devices, sensors, and secondary batteries, among others [1]. These properties include color changes, conductivity changes, redox charge reactions, etc. [1]. The color changes are often due to differences in oxidized and reduced states due to the population of radical (polaron) species in the polymeric backbone.

Among the conductive polymers, polyaniline (PANI) is one of the most promising for practical applications because of its easy preparation, thermal stability and stability in air and water. It is well known that PANI contains spin species such as radicals. If the radicals in PANI could be stably arranged to form a regular array, PANI would exhibit magnetic properties and could be available as an organic magnet. It is relatively straightforward to prepare PANI by either electrochemical or chemical polymerization of aniline in essentially any acidic solution. Unfortunately, PANI does not grow in a regular array of radical species, thus it shows no magnetic properties.

Many magnetic composites have been prepared using PANI and magnetic inorganic compounds such as  $\text{Fe}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4$ , which PANI is mainly employed as support [2–10]. Papers dealing with magnetization of PANI itself are very limited. In 1988, Miyazaki obtained special

PANI films exhibiting magnetic properties [11]. He prepared monolithic PANI films and added cross-linking agents such as pyromellitic anhydride. By swelling and elongating the films in an organic solvent, the film exhibited a relatively large magnetic hysteresis loop. On the other hand, it is suggested that if the repeat unit of polymer has *meta*, *para* coupling, it can yield a ferromagnetic spin alignment upon doping [12, 13]. At low temperature, a weak ferromagnetic exchange interaction is observed between the spins of oxidized meta-PANI [14]. Moreover, Wienk and his co-workers have specially identified PANI with its *meta*- and *para*-aniline oligomers as building blocks for ferromagnetic exchange [15]. However, these methods consist of several troublesome synthetic steps which do not provide any method to increase the spin density. Recently even without elongation by organic solvents, magnetic properties have been observed for PANIs incorporating organic acceptors such as tetracyanoquinodimethane (TCNQ) [16]. The magnetic properties are believed to be due to effective chemical bonds formed between the TCNQ side chains and the PANI backbone. This seems like a more attractive procedure because the spin density can be increased by the radical species generated on the TCNQ molecules. However, this material has a drawback in that the magnetic properties are not observable until after 3 months have passed. In other words, it takes at least 90 days to form magnetically ordered structures.

Our purpose is to prepare PANI possessing stable magnetic properties without TCNQ. Although we did not previously investigate magnetic properties, we have already demonstrated that PANIs quickly and steadily incorporate several quinones when they are electro-oxidized [17–20].

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Recently, we briefly reported that PANI is weakly magnetized by electro-oxidation of PANI in the presence of chloranil (CHR) [21]. In this paper, the incorporation of CHR is carried out. The electrochemical behavior of PANI in the presence of CHR reveals that the quinone electronically interacts with PANI. The quinone is incorporated into PANI during electrochemical oxidation. Measurements of electron spin resonance (ESR) spectra and magnetic susceptibility ( $\chi_g$ ) indicate that the incorporation of the quinones magnetize PANI. Although PANI incorporating CHR shows no ferromagnetic properties, it does exhibit unusual paramagnetic properties.

## 2. Experimental details

All chemicals were of reagent grade. Aniline (Sigma-Aldrich Co.), used as a monomer, was distilled under reduced pressure. The quinones, CHR (Tokyo Chemical Industry Co.), were used after recrystallization from ethanol. Acetonitrile, ethylacetate and tetrahydrofuran (Sigma-Aldrich Co.) were used as organic solvents after distillation under reduced pressure. Inorganic chemicals were analytical grade and used as received without further purification.

A standard three-electrode cell was employed for most electrochemical measurements. This cell comprised a Pt disk electrode with an electrode area of 0.196 cm<sup>2</sup>, a commercial Ag/AgCl electrode and a Pt plate counter electrode with an electrode area of ca. 18 cm<sup>2</sup>. The Ag/AgCl electrode was connected to the cell by means of a salt bridge filled with a saturated KCl aqueous solution. The solution level in the Ag/AgCl compartment was kept below the level in the test cell to prevent contamination by chloride ions. In measurements carried out in non-aqueous solution, the Ag/AgCl electrode was directly soaked in

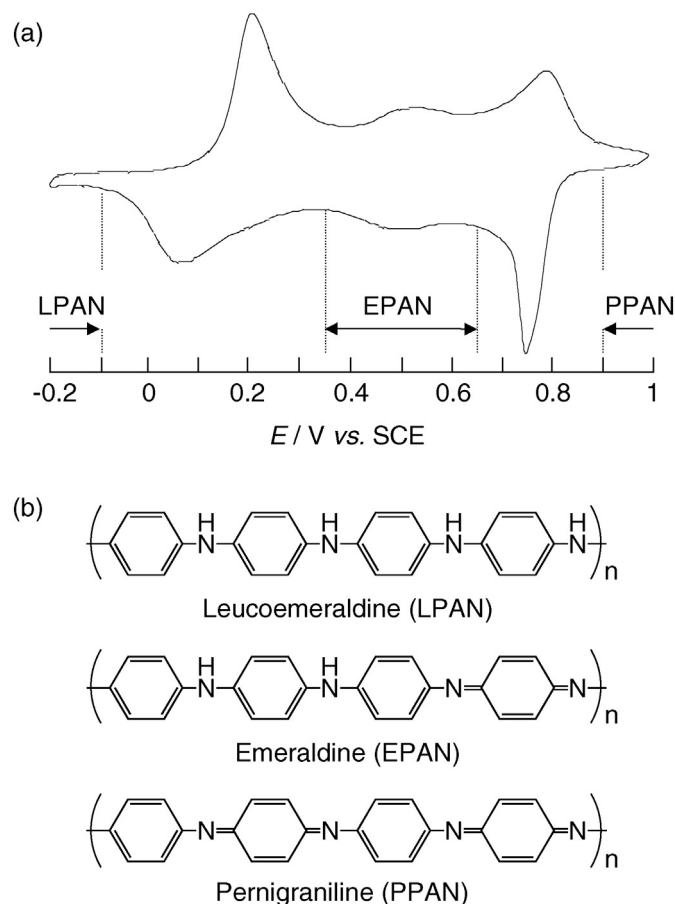


Fig. 1. (a) Cyclic voltammogram at 0.1 V·s<sup>-1</sup> showing the redox activity of PANI in 0.1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. (b) The three main oxidation states of PANI.

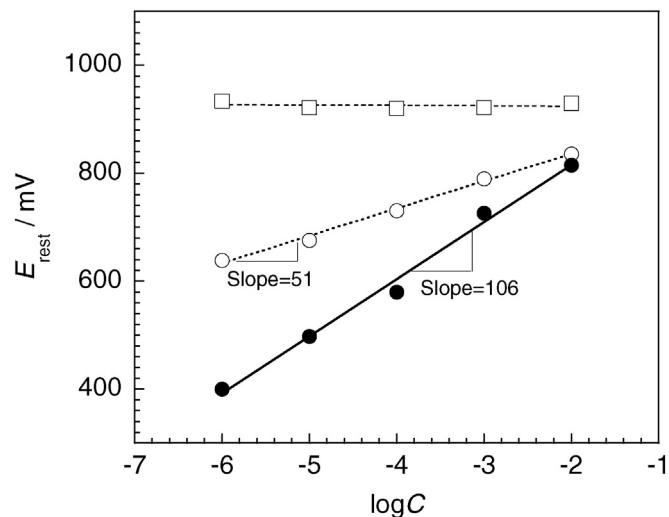


Fig. 2. Nernstian response of PANI to dissolved CHR: PPAN (---), EPAN (.....), and LPAN (—). The rest potential ( $E_{\text{rest}}$ ) was measured in acetonitrile solutions containing 0.1 M NaClO<sub>4</sub> as an electrolyte and CHR at the following concentrations (C):  $1.00 \times 10^{-6}$ ,  $1.00 \times 10^{-5}$ ,  $1.00 \times 10^{-4}$ ,  $1.00 \times 10^{-3}$  and  $1.00 \times 10^{-2}$  M.

the solution. A new Pt plate electrode with an electrode area of ca. 8 cm<sup>2</sup> was employed as the test electrode to prepare PANI powder samples for magnetic measurements. Prior to use, the Pt disk and plate electrodes were treated with aqua regia for 30 s and then polarized by repeated potential cycling between -0.2 and at 1.2 V vs. Ag/AgCl in 0.1 M (1 M = mol·dm<sup>-3</sup>) H<sub>2</sub>SO<sub>4</sub> aqueous solution until the voltammogram showed features associated with hydrogen adsorption/desorption and oxide formation/removal [22]. When the absorption spectra of the PANI films were measured, the PANI films were electrodeposited on a transparent electrode comprised of indium-tin oxide (ITO) coated glass plates 0.8 cm wide and 5 cm long. Prior to use, the ITO electrodes were treated with acetone and then washed in distilled water with an Iuchi US-1 ultrasonic cleaner. The electrochemical experiments were carried out using a Hokuto Denko HZ-3000 potentiostat connected to a personal computer and a Rikadenki RY-101 x-y recorder. The

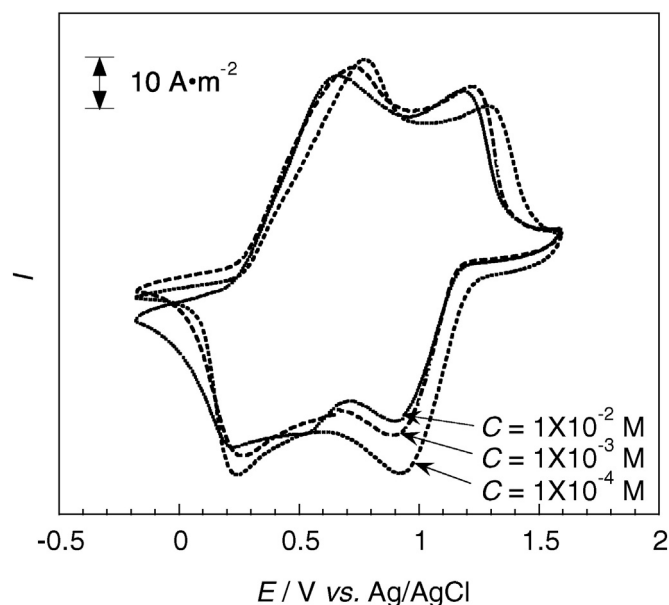


Fig. 3. Cyclic voltammograms of PANI at 0.1 V·s<sup>-1</sup> in three acetonitrile solutions containing 0.1 M NaClO<sub>4</sub> as an electrolyte and the following concentrations of CHR (C):  $1.00 \times 10^{-4}$ ,  $1.00 \times 10^{-3}$  and  $1.00 \times 10^{-2}$  M.

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