SHORT COMMUNICATIONS

A New Technique to Study Kinetics of Chain Conformation in Polyaniline Films

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Conducting polymers are well known to expand/contract upon electrochemical oxidation/reduction. Such dimensional changes induced by an electrochemical stimulus originate from incorporation of solvated dopant ions into the film and/or conformational change of π-conjugated polymer chains. An increasing number of studies have been devoted to the potential-induced deformations of conducting polymers in an effort to fabricate novel actuators and artificial muscles.[1–5] Polyaniline (PANI) and its derivatives are a family of conducting polymers that exhibit a significant extent of deformations at low voltages. They have been intensively studied by Kaneto et al. as a key element of soft actuators.[6–10] Recently, we have found a new type of a potential-induced change in film property of PANI and its derivatives, i.e., a change in the intensity of light reflected from the polymer-coated electrode with an applied potential.[11,12] The change in reflection was interpreted as below. In the reduced state of the PANI film where polymer chains have a coiled structure,[13,14] a light scattering or a diffuse reflection takes place in the polymer layer and thus a negligible intensity of light reaches the photodetector placed at a right position of specular reflection. By increasing the potential, polymer chains stretch and the coiled structure relaxes as has been demonstrated by MacDiarmid and Epstein.[13,14] Consequently, Rayleigh or Mie scattering is attenuated in the polymer film and the incident light can go deep into the polymer layer to reach a highly reflective Pt surface. Then, specular reflection at the Pt surface occurs effectively and the reflected light gains its intensity. When the potential is raised further, the PANI film turns a blue-black color. At the higher potentials, therefore, the PANI film starts to absorb the incident 633 nm light and the intensity of light coming to the Pt surface reduces. In the present study, a new method for investigating kinetics of chain conformation for the PANI film is proposed on the basis of the in situ reflection technique.

Aniline of reagent grade from Aldrich was distilled under Ar atmosphere and stored in a Schlenck tube filled with Ar gas. PANI was deposited on Pt-coated glass plates by a potential-sweep method with 1.3 M aniline in 2.3 M perchloric acid ($HClO_4$). Electrode potentials were referred to Ag/AgCl/NaCl(satd.). After polymerization by cycling the potential between -0.1 and $0.9\,V$ at $50\,mV\,s^{-1}$, the PANI film was rinsed thoroughly with distilled water, dried in air lightly, and trans-
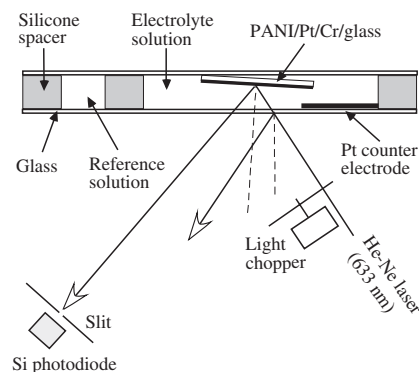

Figure 1. Schematic illustration of an optical arrangement for the in situ reflection measurements.

ferred to a thin layer cell of Figure 1 for in situ reflection measurements. Thicknesses of PANI films were evaluated by measuring the amount of electricity during a potential-step doping in $HClO_4$. The oxidation level was defined as the number of unit charges per aniline unit and calculated from the polymer weight, a molecular weight of an aniline unit, and the doping charge. In situ reflection technique with a He-Ne laser (633 nm) is described earlier.[11,12] The optical arrangement is schematically depicted in Figure 1, where the PANI electrode is slightly tilted from the two parallel glass plates to avoid a light reflected directly at the front glass surface. A current signal of a Si photodiode was converted to a voltage using a current/voltage preamplifier and the voltage signal was fed to a lock-in amplifier. Before starting measurements, the potential of the PANI electrode was kept at a sufficiently negative potential so as to obtain a reduced form of PANI, i.e., leucoemeraldine. Just prior to the measurement, the system was switched to a galvanostatic mode and a constant anodic current was applied to the electrode. A time course of the intensity of a reflected light was measured till the electrode potential reaches 0.5 V. The electrode potential was rested at $-0.2\,V$ till the cathodic current density fell down to -0.2 $\mu A\,cm^{-2}$ or below. Then the next current pulse was applied to the PANI electrode.

Figure 2 depicts a set of light intensity vs. charge curves for a PANI film in $HClO_4$ (pH 1) obtained in the galvanostatic
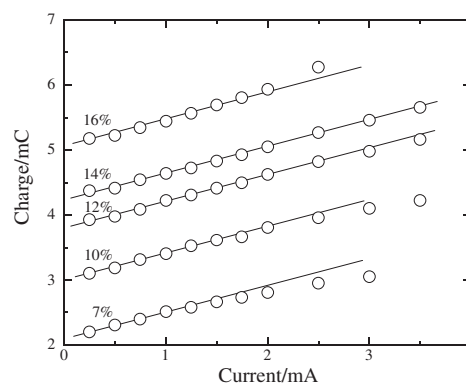
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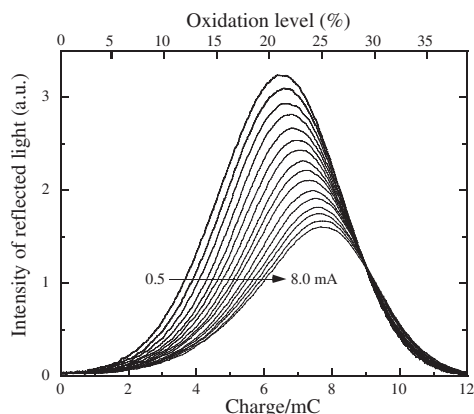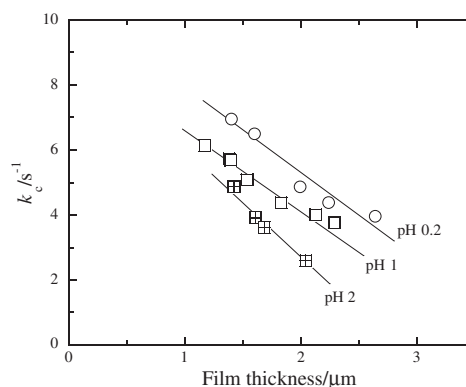
Figure 2. Changes of intensities of 633 nm light reflected on the PANI film of 2.3 μm thickness in HClO₄ (pH 1) with the amount of charges in the current-step experiments with different currents. For clarification of the figure, only the curves obtained with the applied currents of 0.5 to 8.0 mA with a current interval of 0.5 mA are illustrated.

Figure 3. Plots of charge *vs.* applied current at the respective oxidation levels to evaluate the rate constant of the conformational change for PANI film in HClO₄ (pH 1). Numerals near the respective plots denote oxidation levels of the PANI film.

Figure 4. Dependences of k_c value on thickness of PANI film in HClO₄ solutions of different pHs.

mode with varying applied currents. The state of a chain conformation should be controlled by the amount of charges or more explicitly the oxidation level. Therefore, the same charge will give the same light intensity irrespective of the applied current or the rate of polymer oxidation, if the response of a chain conformation to the electrochemical stimulus is sufficiently fast. This implies coincidence of the curves obtained at different applied currents for the fast limit of chain conformation. It is clearly seen, however, that the rising portions of the curves shift to the right as the currents applied to the PANI film are increased. The observed shift of these curves demonstrates a delay in response of chain conformation to an electrochemical oxidation of the PANI film, demonstrating that the rate of a conformational change of polymer chain is within an accessible limit of the proposed *in situ* reflection technique. On the other hand, the descending portions of the curves merge into a single curve. The coincidence of the descending portions is a matter of course in view of the fact that coloration of the PANI film responsible for absorption of the incident light and thus attenuation of the reflected light intensity should occur much faster than the time scale of the current experiments.

Analysis of the light intensity data of Figure 2 is performed in the following way. A given intensity of reflected light corresponds to a certain state of chain conformation. We will draw a straight line parallel to the abscissa axis and read the charges at which the straight line intersects with the respective curves. Thus obtained charges are plotted against the currents corresponding to the curves of Figure 2. Figure 3 shows charge *vs.* current plots evaluated at different oxidation levels. The slope of the plot represents a time constant characteristic of the rate of a conformational change in the PANI film and its inverse gives a rate constant for this process (k_c). All the plots fit straight lines with almost the same slope values except for in the high current region. The slopes yield $2.4 \, s^{-1}$ for the k_c value of the PANI film in HClO₄ (pH 1). The rather small k_c value suggests that PANI chains in the electropolymerized film as thick as 2.3 μm are folded and intertwisted, so that loosening of their conformations upon oxidation may not be readily attained. Figure 4 depicts plots of k_c *vs.* thickness of PANI film in HClO₄ solutions of pH 0.2, 1 and 2. It is seen that a decrease in pH of the solution leads to greater k_c values. On the other hand, by increasing the film thickness the k_c values

tend to decrease in common for each solution. The decrease in k_c with film thickness is in accord with the view that the rate constant of the conformational change is controlled primarily by tangling of polymer chains.

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