Potential-step response of absorption at conducting-to-insulating conversion of polyaniline films for demonstrating the slow relaxation

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Abstract—Absorption of polyaniline films responding to a potential step from a conducting state to an insulating state showed linear variations with logarithmic electrolysis time when the stepped potential \( E \) was less than the percolation threshold potential \( E_c \). Then the slope of the linear relation varied with \( E \). The observation demonstrates more directly the slow relaxation than the time-dependence of the voltammetric peak potentials or the charge reported previously. The relaxation of the absorption is also more essential in the faradaic process than measurements of currents or potentials because it includes no capacitive contribution. Comparison of the current-time curve with the time-derivative of the absorption showed that most of the current before 0.5 s was capacitive due to the charging of the double layer. The capacitance vs \( E \) curve was linear for \( E > E_c \) whereas it deviated from the proportionality for \( E < E_c \). This behavior reflected on whether the anodic voltammetric peak appeared or not when the initial potential was less or more than \( E_c \).

Key words: slow relaxation, conducting polymers, polyaniline films, relaxation of absorption, logarithmic time-dependence.

INTRODUCTION

An electrical conducting polymer changes between an insulator and a metal-like conductor by an electrochemical control [1, 2]. Since the repeatability by the electrochemical switching is so excellent that the polymers have been applied to secondary batteries, the response looks reversible [3]. However, responding rates as short as a few microseconds vary with the switching directions [4–8]. Responses on the hours scale also show hysteresis in curves of some physical variables vs the electrode potentials [9–16]. These data suggest involvement of apparent irreversibility in the switching over the time-window of \( 10^6 \). The irreversibility may have latent effects on switching functionalities of the polymers [7]. A model of the insulating-to-conducting conversion has been described by the propagation theory of a conducting zone [17, 18], in which the conversion occurs at the well-defined boundary [19–21] between the insulating zone and the conducting zone. It has been demonstrated quantitatively in videoscopic measurements, leading to evaluation of the propagation rate [21]. In contrast, the conducting-to-insulating conversion occurs uniformly without any definite boundary [22, 23], and is associated with not only electrochemical slow relaxation [24, 25] but also slow ESR response [26]. Unfortunately, the mechanism is still under debate.

The slow relaxation is a linear relation of anodic voltammetric peak potentials and currents with the logarithmic electrolysis time of the reduction before the potential scan [27, 28]. It is called a memory effect [29]. Since the voltammetric potential and current involve kinetic effects, more reliable data lie in the relation between the amount of charge and the time. The charge has also showed the logarithmic dependence [30, 31]. A proposed mechanism of the dependence is the kinetics in which conducting clusters which have lost conducting paths toward the electrode recover a conducting path by thermal rearrangement of the clusters [31].

A critical difficulty in electrochemical measurements is involvement of large capacitive current [32]
because of formation of the double layer around fibril-like polymer surfaces [33]. It is expected that optical detection allows us to exclude the capacitive contribution from the response [34, 35]. It has been reported [35] that a larger potential step makes a more distinctive difference between the amount of the charge and the optical absorption. In this report, we measure time-dependence of absorption at polyaniline films in the course of conducting-to-insulating electrochemical conversion in order to evaluate accurately the amount of the conducting species.

EXPERIMENTAL

The potentiostat was home-made, controlled by a personal computer. The spectroscopy used was JASCO V-570. The electrochemical cell was a spectroscopic holder, into which an indium tin oxide (ITO) plate of a working electrode, a platinum coil of a counter electrode and a saturated calomel electrode were inserted. The active area of the working electrode (25 mm²) was minimized by shielding the surface with tape in order to suppress ohmic potential drop. A use of thin films was also effective for decreasing the ohmic drop.

Polyaniline films were electrochemically synthesized on the ITO electrode potentiostatically at 0.8 V vs sce in 0.1 mol dm⁻³ (M) aniline and 1.0 M H₂SO₄. They were rinsed well with sulfuric acid and transferred into the electrochemical cell. From the correspondence of the amount of cyclic voltammetric charge at 0.9 mC mm⁻¹ with the thickness 1.0 μm of the film [23, 36], the thickness of the film was estimated to be ca. 90 nm.

Since the ITO electrode was unstable in a strong acid after a few hours’ use, a series of potential step experiments was made during 20 min. Application of 0.6 V for 30 s was enough to reach the steady conducting state because of the rapid insulating-to-conducting conversion [23]. We confirmed that the response to the given potential step was reproduced after a series of experimental runs.

RESULTS AND DISCUSSION

It has been recognized that the conducting species of polyaniline shows a broad absorption band between 650 nm and 900 nm [37]. Since relaxation curves of absorption at 650, 750 and 850 nm were almost the same in shape, we used absorption data at 750 nm for detailed experiments. Potential 0.6 V vs sce was at first applied to the electrode for 30 s to make the film conducting. When it was stepped to several values of E less than 0.5 V vs sce, the absorption decreased rapidly, reaching an apparently constant value. The responding current measured simultaneously showed a decay curve.

We consider correspondence of the absorption-time curve with the current-time curve. Faradaic charge should generally have a linear relation with absorption strength of the redox species if the redox species is immobilized uniformly on the electrode. Thus the faradaic current should agree with the time-derivative of absorption through a linear transformation. If current at a potential step includes a capacitive component, any linear transformation does not fit the current to the time-derivative of the absorption. However, the current at a long time may be overlapped with the time-derivative of the absorption because the capacitive current vanishes long after the potential step. Figure 1 shows the chronoamperometric curve and the time-derivative of the absorption of which the ordinate was adjusted so that the two curves at a long time were overlapped (see the expanded ordinate on the left side). The agreement for the long time was fairly good at every stepped potential ranging from −0.10 to 0.45 V vs sce.

Let t₀ be the time after the two curves begin to merge in Fig. 1. Then the area encircled with two curves for t < t₀ stands for the capacitive charge:

\[ q_{CG} = \int_0^{t_0} [I - k(dA/dt)] \, dt, \]

where k is a constant common to all the curves at different stepped potentials, E. The value of t₀ was 0.46 ± 0.03 s in all the potential domain. If the amount of q₁ is charged to a conventional capacity C, it should be expressed by \( q_{CG} = C \Delta E \), where \( \Delta E \) is the potential step width from 0.5 V vs sce to E. It has been pointed out [35] that a large potential step makes the capacitive effect remarkable. Figure 2 shows variation of \( q_{CG} \) with \( \Delta E \). Excellent proportionality in the domain \( \Delta E < 0.5 \text{ V} \) or \( 0.5 > E > 0.2 \text{ V} \) vs sce indicates a potential-independent capacitance.

![Fig. 1. Curve (dashed) of dA/dt fitted to the chronoamperometric curve (solid) for t > 0.4 s when the potential was stepped from 0.5 V to 0.2 V vs sce in 1.0 M H₂SO₄, where t is the time after the potential step. The absorption was observed at 730 nm. The left ordinate was expansion of the right one.](image-url)
The increase in $C$ for $E < 0.2\,\text{V vs SCE}$ is ascribed either to an increase in the permittivity or an increase in the area of the capacitance. Specific adsorption of polyaniline at $E < 0.2\,\text{V vs SCE}$ might lead to a decrease in the permittivity, as is the case for the conventional adsorption on a platinum electrode. It is known that fractal surfaces are formed \[38\] to increase the surface area more than that predicted from a molar fraction of a conducting species \[22,39\] near a percolation threshold potential, $E_c$ \[21,40\]. The reported value of $E_c = 0.2\,\text{V vs SCE}$ is very close to the potential at which the plot deviates from the line in Fig. 2. Therefore the increase in the capacity is probably ascribed to the fractal effect.

The time- and potential-dependent absorption was normalized with the absorption between $-0.1$ and $0.5\,\text{V}$. The normalized absorption vs time curves were almost identical with time-variations of the faradaic charge extracted from chronocoulometric curves. Figure 3 shows plots of the normalized absorption against $E$ at some lapses after the potential step. As the time lapses, the sigmoidal curves become steeper, the lower part of the curve shifting in the positive direction. A similar shift was observed in the potential-dependence of ac amplitude at the negative potential sweep in the attempt of determining $E_c$ \[40\]. A Nernst log-plot was made, of which the slope gave the number of electron $n$ from $0.19$ to $0.21$. Even the curve at $50\,\text{s}$ has not reached the quasi-steady state value, $n = 0.3$. This behavior is nothing but the slow relaxation.

Variations of $A$ with the logarithmic time are shown in Fig. 4. Plots for $t > 1.0\,\text{s}$ fell on a straight line although the logarithmic time-domain with the linearity is narrower than the domain of a few hours in the previous experiment \[31\]. Slopes of the lines are almost zero for $E > 0.2\,\text{V vs SCE}$, indicating that the relaxation ceases at $1.0\,\text{s}$. In other words, the reduction at $E > 0.2\,\text{V vs SCE}$ is completed in $1.0\,\text{s}$. It is for $E < 0.2\,\text{V vs SCE}$ that the conducting-to-insulating conversion obeys the logarithmic relaxation. The time at which plots begin to be on the line gets longer as $E$ becomes negative for $E < 0.2\,\text{V vs SCE}$, as shown by the dotted line in Fig. 4.

According to the theory proposed for the logarithmic relaxation, the charge of the conducting species left in the film is expressed by \[31\]:

$$ q = q_T \left( \frac{1}{a} \ln t \right. + \left. \frac{1}{a} \ln \frac{ak_s}{q_T} + 1 \right), \quad (2) $$

where $q_T$ is an amount of all the redox charge, $s_0$ is the average size of conducting clusters at $E = E_c$, and $a$ is a constant. This has been derived by combining the size of conducting clusters with the first order kinetics. The intercept of the straight line in Fig. 4 is not relevant to the slow relaxation because it is mainly controlled by the process immediately after the potential step. Instead, it is the slope $(q_T/a)$ that
expresses the slow relaxation. Variation of the slope with the potentials is shown in Fig. 5. The slope changes drastically at $E = 0.19 \, \text{V vs SCE}$ which is very close to $E_c$, as is the case for $q_E$ in Fig. 3. Dependence of $a$ on $E$ suggests an insufficiency of equation (2). It can be explained qualitatively by dependence of size of the conducting clusters on $E$, because more resistive film (at more negative potential) may have fewer and smaller conducting clusters. The effect of the slow relaxation may be manifested to the variation of cyclic voltammetric waveform with the initial potential. Figure 6 shows the variation in which various values of the initial potential $E_i$ were applied to the conducting film for 100 s and then the potential was swept in the positive direction. The voltammograms (a)–(d) at $E_i < E_c$ showed a well-defined peak whereas there is no peak in waves (e)–(g) for $E_i > E_c$. A simple reversible couple should manifest a peak at ca. $0.27 \, \text{V vs SCE}$ for any value of $E_i$ less than the peak potential. Thus, the appearance of the peak in the restricted domain ($E_i < E_c$) suggests that the reduction at the initial potentials less than $E_c$ should be responsible for the exhibition of the peak.

CONCLUSION

The conducting-to-insulating conversion at $F > F_c$ is completed in 1 s without any slow relaxation. In contrast, the conversion at $E < E_c$ is associated with the logarithmic time-variation after the uniform rapid conversion. The conversion rate is critically changed at $E = E_c$. The percolation transition is reflected in the conversion rate as well as the growth of the conducting zone at the insulating-to-conducting conversion. The slope of the linearity in the $q$ vs $\ln t$ curve varied with $E$, although quantitative discussion has not yet been given to it.

Double layer-charging currents at a short time were evaluated from comparison of the chronoamperometric curves with the time-derivative of the absorption-time curves at the potential domain from $-0.1$ to $0.45 \, \text{V vs SCE}$. The double layer charge for $E > E_c$ was proportional to $\Delta E$. It deviated positively from the linearity when $E < E_c$. The nonlinearity of $C$ with $\Delta E$ may be ascribed to formation of the fractal structure of the conducting species.

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