

Scaling Property in Surface Growth and Mole Ratio of Dopant to Pyrrole in a Conducting Polypyrrole Film Generated by Electropolymerization

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The surface morphology of sodium p-toluenesulfonate-doped polypyrrole films generated by electropolymerization is investigated using a laser confocal scanning microscope. The surface growth of the polypyrrole film comprising grains exhibits a scaling behavior characterized by the dynamic exponent, $z=1.61$, the roughness exponent, $\alpha=1.0$, and the growth exponent, $\beta=0.65$. The value of β greater than 0.5 suggests the presence of local effect such as interplay between the grains in growth. In addition, the mole ratio of dopant (sodium p-toluenesulfonate and phosphoric acid) to pyrrole in the polypyrrole film is found to be determined by a simple method based on the deposit mass measurement of the polypyrrole film using an equation derived from two charge transfer reactions that describe the electropolymerization and oxidation process of pyrrole and doping agent. Using the simple method, the mole ratio and the electrical conductivity of the sodium p-toluenesulfonate-doped polypyrrole film are shown to be linearly proportional to the deposition rate.

Keywords: pyrrole, dynamic scaling, surface growth, doping agent, mole ratio, electropolymerization

1. INTRODUCTION

Polypyrrole films have attracted researchers in science and technology because of their stability in oxidized states and use in a large field of application such as biosensors [1-2], gas sensors [3], chemical sensors [4], microstructures [5-6], and display devices [7].

Synthesis of the conducting polypyrrole film is often carried out by electropolymerization using a solution including a doping agent such as phosphoric acid [8], sodium dodecylbenzenesulfonate [9], and sodium p-toluenesulfonate [10]. Many studies indicate that as an

anode electrode on which the polypyrrole film is deposited, inert electrodes [11] (ITO glass, Pt, and Au) have an advantage over common metals [12] (Fe, Al, and Cu) because of no passivation required for electropolymerization.

In recent years, many theoretical and experimental studies [13] on the kinetic surface roughening in deposition have revealed the simple scaling relation that the standard deviation of a film height, $w(L, t)$ obeys a relationship within the framework of normal scaling, $w(L, t) \sim L^\alpha f(t/L^{\alpha/\beta})$ where L indicates a system size at time t , α is the roughness exponent, and β is the growth exponent. The values of α and β are insensitive to experimental details in the system. These scaling exponents determine a universality class characterizing the scaling behavior in surface growth. However, there have been very few studies on the scaling behavior of polypyrrole films in surface growth [14].

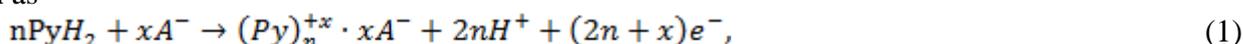
The composition of the doped polypyrrole film, especially the mole ratio of dopant to pyrrole is of importance to understand the mechanism of electric conductivity [15] and electrochemical reactions [5] in electropolymerization. One of the primary hindrances to investigate the mole ratio is that the polypyrrole film has too little or no solubility in inorganic or organic solutions. Therefore, physical properties of the polypyrrole films as being related to the feeding content of doping agent in a pyrrole solution have been discussed [16-17]. On the other hand, the mass of polypyrrole films produced by electropolymerization is directly involved with the mole ratio. For example, when the mole weight of a doping agent is heavier than that of pyrrole, an increase in the mole ratio simply causes a change in the mass of the polypyrrole film. Hence, the change in the mass of the doped films will enable us to determine the mole ratio.

The purposes of this study are to report that the surface growth of the doped polypyrrole film obeys the anomalous scaling law that indicates the growth exponent of β greater than 0.5, and that the mole ratio of dopant to pyrrole in the polypyrrole film electropolymerized at a fixed current density is simply determined using the deposit mass measurement of the doped polypyrrole film.

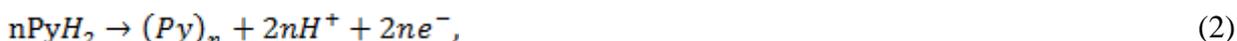
2. EXPERIMENTAL SETUP

A carbon and ITO glass plate (6 Ω as a sheet resistance and the rms roughness of 1.2 nm) of 30x10 mm² each were prepared for a cathode and anode electrode. As the ITO glass is not needed to form a passivation layer, the stable electropolymerization proceeds. The two electrodes cleaned by a wet process were placed parallel to each other in a quiescent electrochemical cell filled with an aqueous solution including the following components (molL⁻¹): C₄H₄NH (Pyrrole), 0.2; as a doping agent [8] and [10] CH₃C₆H₄SO₃Na (P-T is used for abbreviation of sodium p-toluenesulfonate), 0.3, and 1; or H₃PO₄ (PA is used for abbreviation of phosphoric acid), 0.2. The solution was kept in a temperature range of 275 to 311 K.

Pyrrole polymerizes on the ITO glass plate by linkage along with loss of a proton. The charge transfer reaction equation for electropolymerization [9,18] and oxidation of a doping agent is simply written as



which comprises



where PyH_2 and A^- are the pyrrole molecule and dopant anion, n is the number of polypyrrole molecule or the degree of polymerization, and x is the mole number of the doping agent. Eqs. (2) and (3) indicate the polymerization of pyrrole and the oxidization process. In Eq. (1), equating the number of moles of product expressed in electrochemical terms with the number of moles of product expressed as molecular weight, we simply have,

$$x/n = (2mF/tI - m_n)/(m_n - mF/tI), \tag{4}$$

where m is the mass of the synthesized polypyrrole film, m_p is the mole weight of Py , m_a is the mole weight of the dopant anion, t is the deposition time, I is the current, and F is the Faraday's constant. The deposition rate, m/t should be in the range of $Im_p/2F$ to Im_a/F . Eq. (4) indicates that the mole ratio, x/n can be determined by the deposition rate, m/t and the current, I .

A fixed current density of 2 mAcm^{-2} applied in this experiment was chosen as follows: Eq. (4) requires the deposition process that obeys only the charge-transfer reactions, in other words, the process can be described only by the Butler-Volmer equation [19]. The current density and potential at the anode electrode were measured in a solution of 0.2 molL^{-1} pyrrole and 1.0 mol L^{-1} P-T using a Luggin capillary containing a KCl solution.

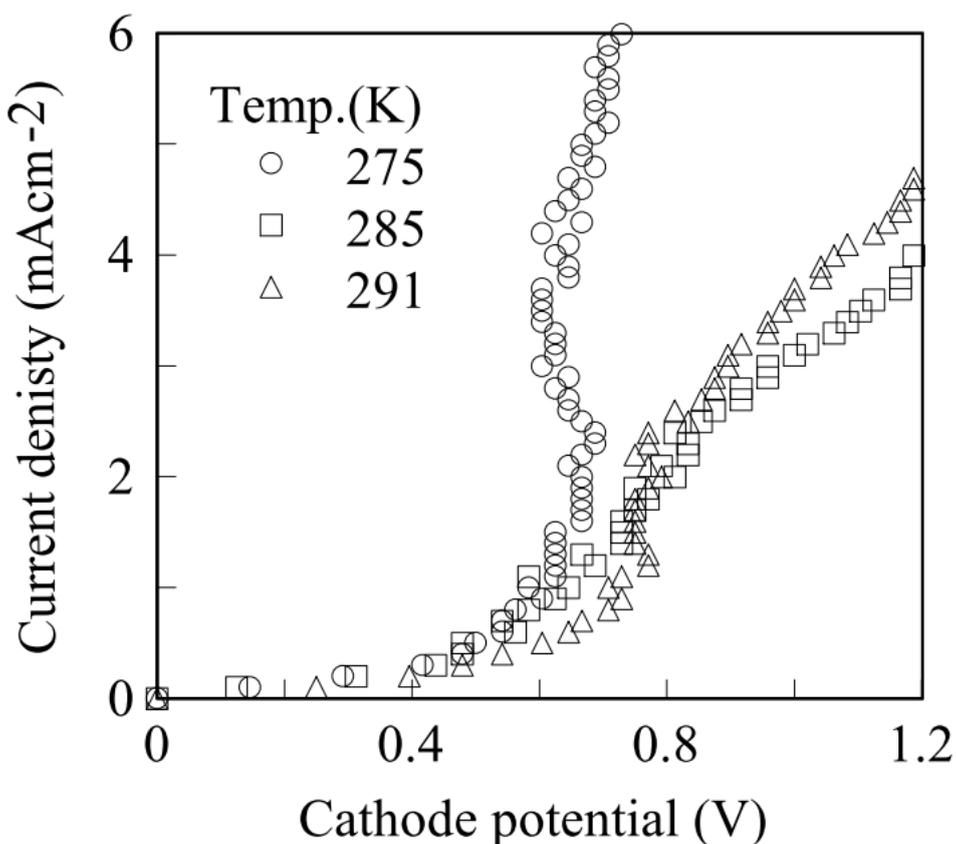


Figure 1. Current and anode potential characteristic measured at a sweep rate of 6 mVs^{-1} in a pyrrole solution including 1 mol L^{-1} P-T.

As shown in Fig.1, the current-potential plot indicates the exponential behaviour expressed by the Butler-Volmer equation in a current range of 0 to 2 mAcm⁻² irrespective of temperature.

After deposition, the polypyrrole film that was rinsed with distilled water and dried was weighed to a precision of 0.1 mg with an electric balance (AND HR-60). The deposited mass, which in this experiment is changed with temperature and the concentration of the doping agent, allows determination of the mole ratio in Eq. (4).

The surface image of the polypyrrole film, which was observed with a confocal laser scanning microscope (Keyence VF7500) having an accuracy to 0.01 μm in height, was stored in a computer.

A four-point probe technique [20] (K&S probe) was used for the measurement of electrical conductivity at room temperature. The electrical conductivity of the polypyrrole film was calculated from a voltage drop linearly proportional to the current passing between two needles in the polypyrrole film.

3. RESULTS AND DISCUSSION

According to the electropolymerization process [9] at the anode electrode, polymerization in Eq. (2) and oxidation in Eq. (3) proceed as follows: A pyrrole monomer oxidized at the ITO glass electrode becomes a radical cation. Next, a dimer comprising such two species and polymeric pyrrole are again oxidized and the propagation of the polymer occurs by addition of the pyrrole radical cation to the polymeric radical cation, which is doped with negative ions called a doping agent. Thus, the charge transfer reactions in Eq. (2) and (3) describe the electropolymerization and oxidization process.

3.1 Surface growth

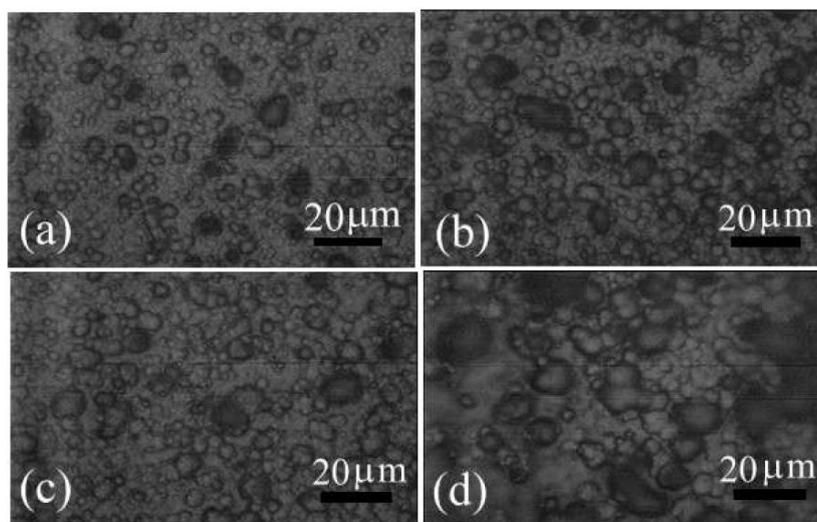


Figure 2. Microscope images of the polypyrrole films electrodeposited for 1500 s at a temperature of (a) 275 K, (b) 279 K, (c) 285 K, and (d) 291 K. The solution including 0.2 molL⁻¹ pyrrole and 1.0 mol L⁻¹ P-T was used.

Figure 2 shows microscope surface images of the polypyrrole films electrodeposited from a solution of 1.0 molL^{-1} P-T for four different deposition temperatures. The surface layer comprising grains appears to be closely packed and relatively smooth. The grain size was measured within a system size, L of 48 to $254 \text{ }\mu\text{m}$.

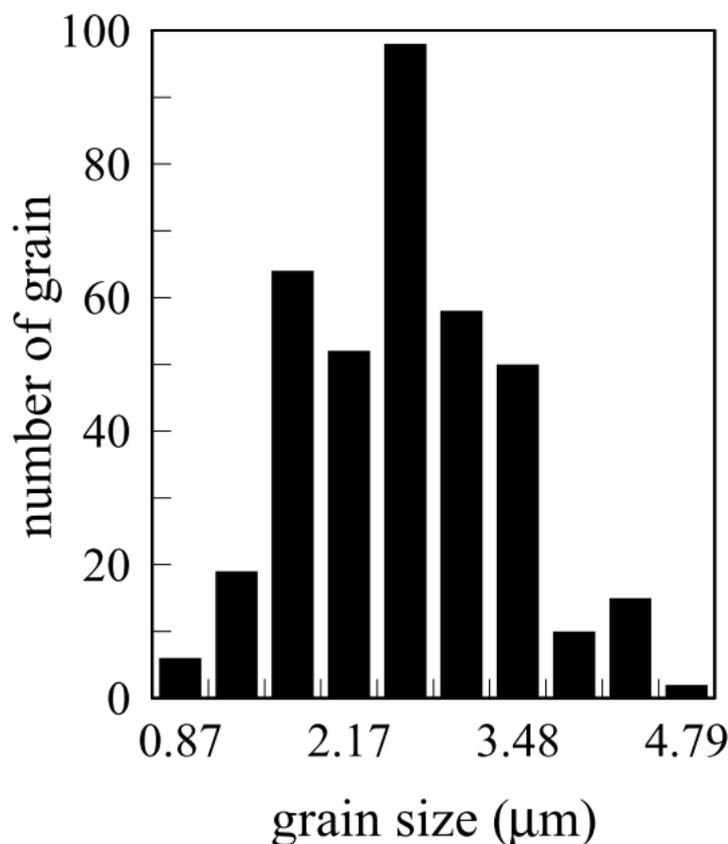


Figure 3. A typical distribution of grain size electrodeposited from the solution including 1 molL^{-1} pyrrole at a temperature of 291 K and a deposition time of 600 s.

The typical distribution of grain size at a deposition time of 600 s and a temperature of 291 K shown in Fig. 3 appears to obey the Gaussian distribution, or Poisson distribution, or Rayleigh distribution, however, it is difficult to choose one distribution function from many similar distribution functions from the viewpoint of data fitting. Hence, we make an attempt to investigate a relationship between the standard deviation of grain size, σ and the average grain size, $\langle R \rangle$ in a growth time range of 300 to 1500 s for temperatures of 275, 279, 285, and 291 K. As shown in Fig. 4, the standard deviation shows a behaviour similar to the average grain size,

$$\sigma \sim \langle R \rangle. \quad (5)$$

In Fig. 5 (a), a log-log plot of the average grain size $\langle R \rangle$ vs. deposition time t is shown. The average grain size obeys a power law of t and the straight line shown in Fig. 5 (a) has a slope of 0.62. On the other hand, a log-log plot of the variance of the grain size, σ^2 vs. t is shown in Fig. 5 (b). The straight line shown in Fig. 5 (b) has a slope of 1.3.

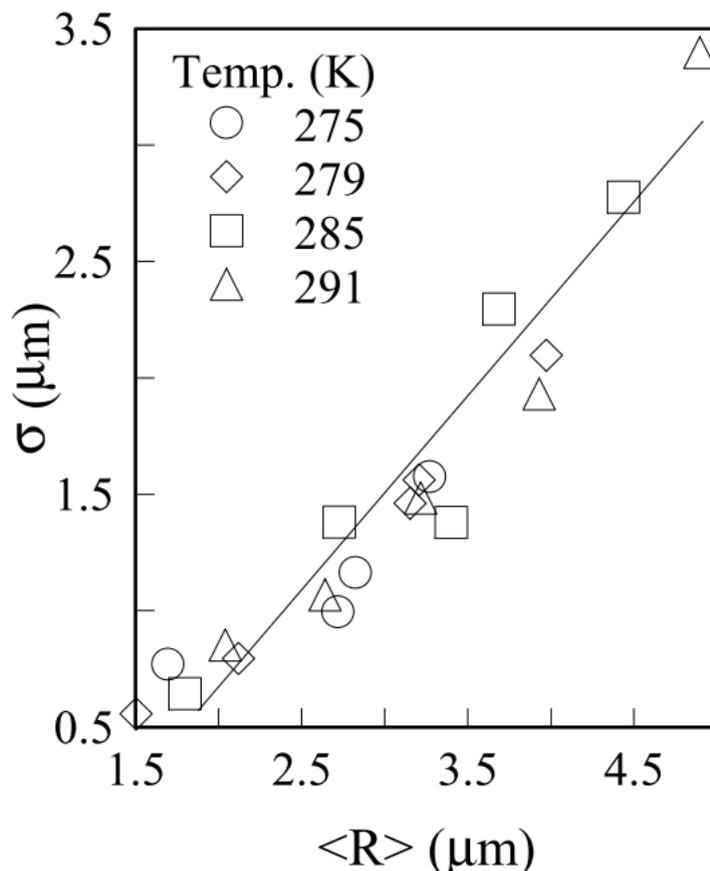


Figure 4. A plot of σ vs. $\langle R \rangle$ for 275, 279, 285 and 291 K in a deposition time of 300 to 1500 s for the solution including 1.0 molL^{-1} P-T.

A fluctuation that plays an important role in phase transition provides useful information about the mechanism of statistical surface growth. For example, as stated in Introduction, the standard variation of surface height in film growth [13], which is a type of fluctuation, is known to obey a power law described by order parameters such as the roughness exponent α , the growth exponent β , and the dynamic exponent $z = \alpha/\beta$ in normal scaling. According to the dynamic scaling theory in surface growth, the correlation length, ξ is related to time,

$$\xi \sim t^{1/z}. \tag{6}$$

The correlation length is defined by the spatial extent of fluctuations in a physical quantity about the average of that quantity. If the correlation length is related to $\xi \sim \langle R \rangle$, we have

$$\langle R \rangle \sim t^{1/z}. \tag{7}$$

where z is called the dynamic exponent. The slope in Fig.5 (a) yields $z = 1.61 \pm 0.07$ for four kinds of temperature. In addition, the variance of grain size σ^2 following the dynamic scaling theory is given by

$$\sigma^2 = \sum (R_i - \langle R \rangle)^2 / N \sim t^{2\beta}, \tag{8}$$

where R_i is the grain size ($i=1, 2, \dots, N$) and N is the number of grain. The slope in Fig. 5 (b) yields $\beta = 0.65 \pm 0.09$. In comparison with Eq. (7), Eq. (8), and $z = \alpha/\beta$, the value of α should be equal to

1. In fact, the value of z and β in this experiment leads to $\alpha=1.05\pm 0.19$ for a temperature range of 275 to 291 K. Hence, Eq. (7) is shown to be valid in this experiment.

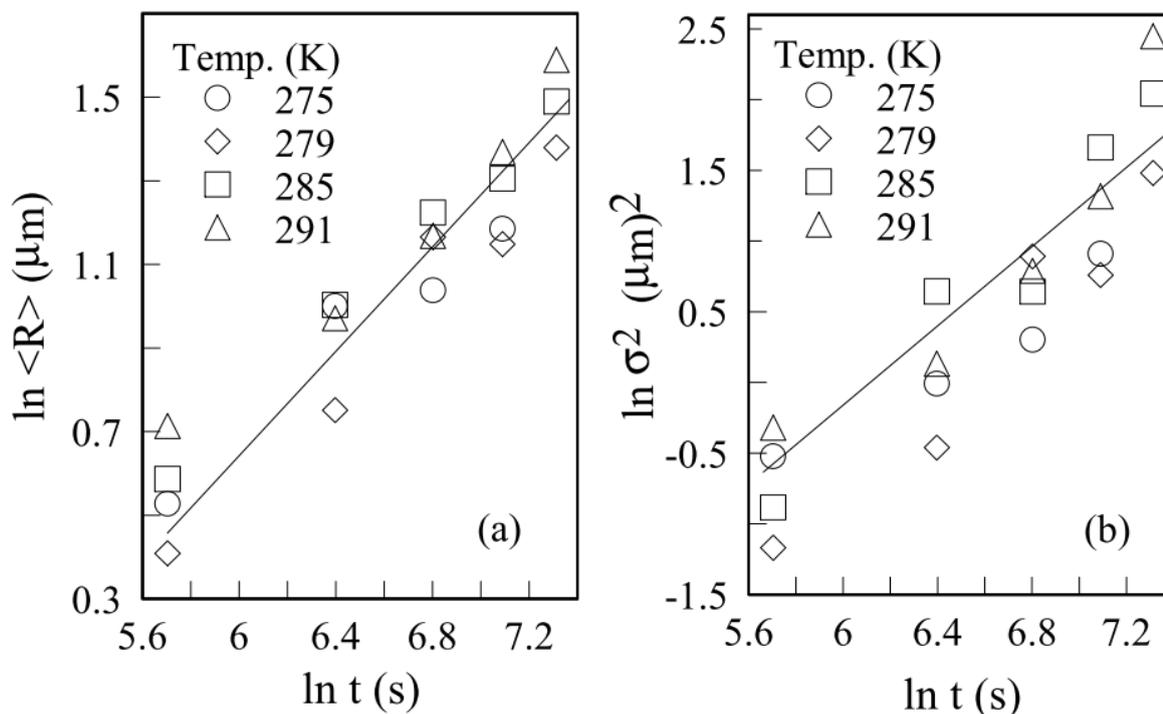


Figure 5. Statistical parameters of grain size -distribution in the polypyrrole film formed from a 0.2 molL⁻¹ pyrrole solution including 1.0 molL⁻¹ P-T. (a) Log-log plot of the average grain size $\langle R \rangle$ vs. time t for four different temperatures. The solid straight line with a slope of 0.62 is drawn to help viewing. (b) Log-log plot of the variance of the grain size σ^2 vs. time for four different temperatures. The solid straight line with a slope of 1.3 is drawn to help viewing.

No statistical surface growth model gives the values of α and β consistent with those in this experiment as long as we know. However, the value of α is almost consistent with that predicted by the surface diffusion-driven growth model [21],

$$\frac{\partial h}{\partial t} = -\kappa \nabla^4 h + \lambda \nabla^2 (h)^2 + F + \eta, \tag{9}$$

where F is the particle flux, η is the random fluctuation in the deposition process, and λ and κ are constants. The exponents α and β are obtained theoretically for two cases in growth on two-dimensional substrates: for $\lambda=0$ and $\kappa \neq 0$ (linear case), $\alpha=1$ and $\beta=0.25$; for $\lambda \neq 0$ and $\kappa \neq 0$ (non-linear case), $\alpha=2/3$ and $\beta=0.2$. The former represents a local diffusion and the latter an intermediate-range diffusion of atoms on the surface. The value of α and β gives a measure of the deviation of grain size and that of the time-development of grain size. The value of β in this experiment is considerably different from that of the model.

The value of β greater than 0.5 [22] is often found in metal electrodeposition, and characterizes the local effect such as surface instability related to the interplay between the grains in growth. Grains in growth competes each other and in the result coalescence may take place. In fact, the coalescence of

two grains is observed in Fig. 2. The pyrrole molecular in the anode substrate moves in a local range of the grain-size, which means the surface growth driven by the coalescence of grain.

3.2 A change in the deposit mass at the fixed current density

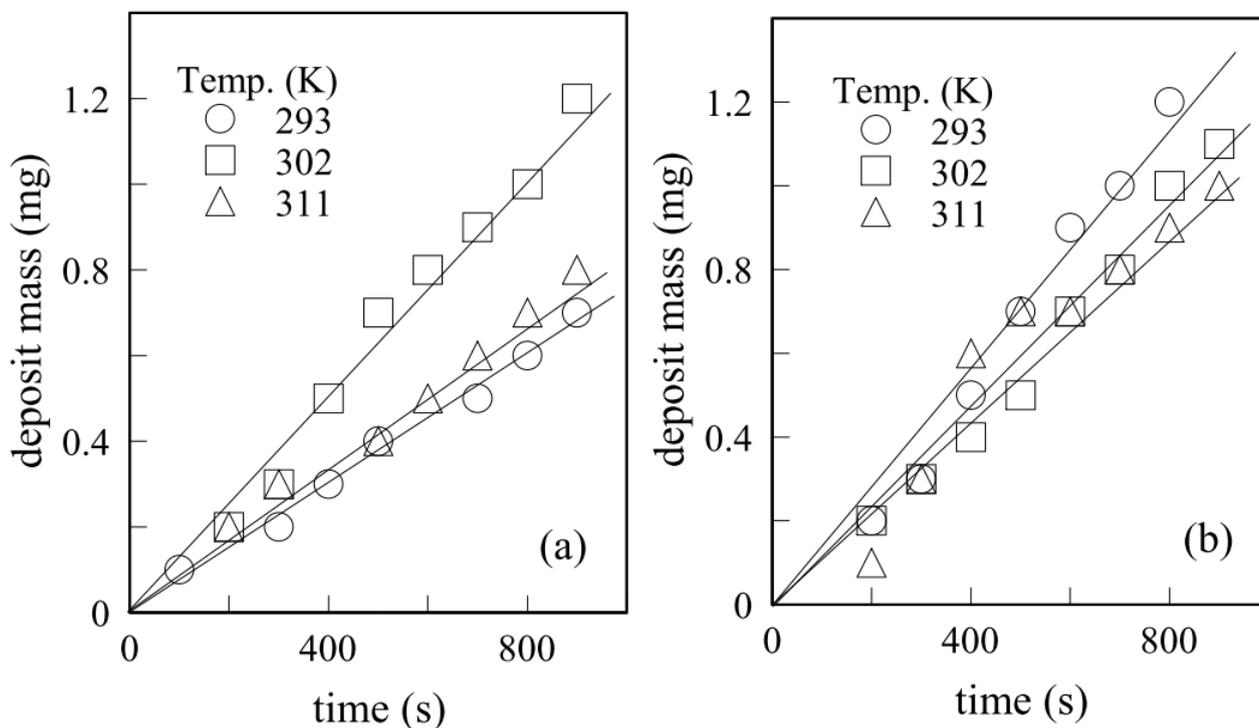


Figure 6. Change in the deposit mass of the polypyrrole film for three different temperatures. (a) 0.2 molL⁻¹ pyrrole solution including 0.3 molL⁻¹ P-T, (b) 0.2 molL⁻¹ pyrrole solution including 1.0 mol L⁻¹ P-T.

Figure 6 shows plots of the deposit mass of the polypyrrole film vs. the deposition time from the pyrrole solution including two different concentrations of P-T. The deposit mass at 2 mA cm⁻² is linearly proportional to the deposition time. The slope of the straight line best fitted to the data in Fig. 4 provides the deposition rate, m/t in Eq. (4). The mass of the polypyrrole film deposited electrochemically from the solution including 0.3 molL⁻¹ P-T is more affected by temperature than that deposited from the solution including 1 molL⁻¹ P-T. In general, the deposit mass at a fixed current density is not influenced by temperature because the current consumed to form an adatom from an ion in the solution obeys the Faraday's law. However, if a molecular weight of doping agent is different from that of pyrrole, the mass of the doped polypyrrole film depends on the mole ratio x/n . Hence, in Fig. 6 the mass of the P-T-doped polypyrrole film, which is affected by temperature, indicates a change in the mole ratio x/n at each temperature.

On the other hand, in Fig. 7, the mass of the polypyrrole film electropolymerized using the solution including PA is shown. The deposit mass at 2 mAcm⁻² is linearly proportional to the deposition time within the margin of error as well as that of the P-T doped polypyrrole film. In

comparison with the mole weight of P-T, the molecular weight of PA is a little larger than that of pyrrole.

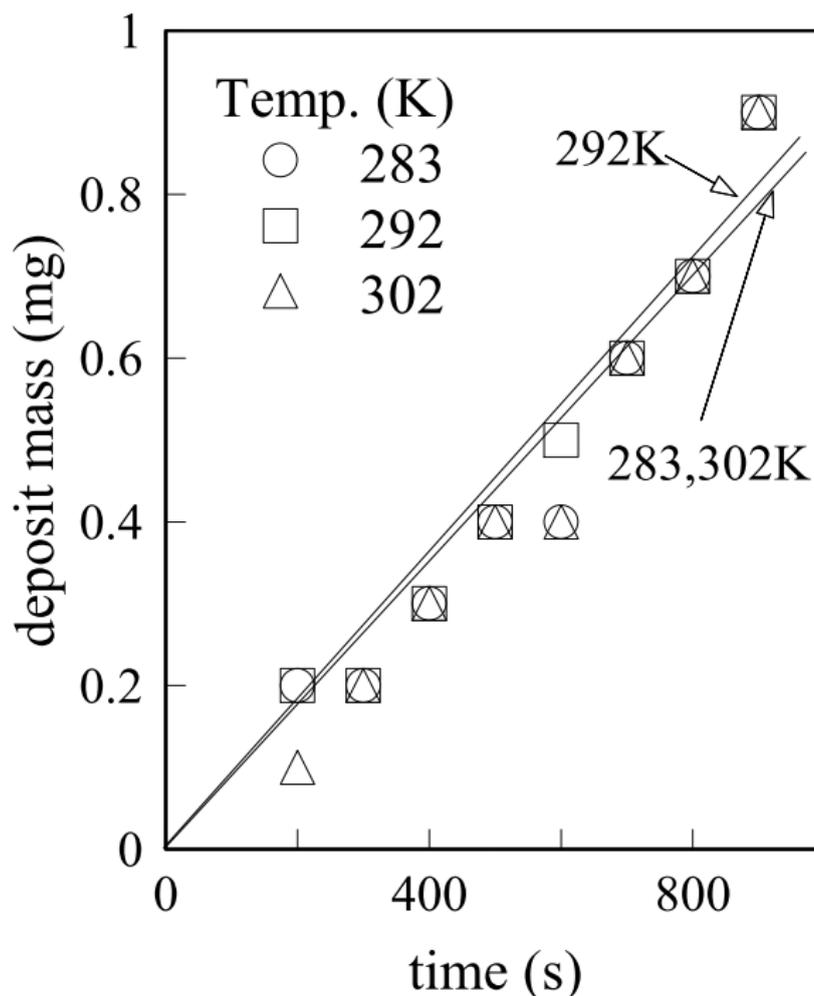


Figure 7. Change in the deposit mass of the polypyrrole film electrodeposited from a 0.2 molL^{-1} pyrrole solution including 0.2 molL^{-1} PA for three different temperatures.

Hence, the deposit mass is not so much affected by temperature and on average lighter than that of the P-T doped polypyrrole film. A change in the mole ratio x/n in Eq. (4) for the PA doped polypyrrole film will remain smaller than that for the P-T-doped polypyrrole film.

3.3 Mole ratio x/n at different temperature

The mole ratio x/n is determined by Eq. (4) using the deposition rate shown in Figs. 6 and 7. Figure 8 shows a plot of the deposition rate vs. the mole ratio for the polypyrrole films doped with PA and P-T for three kinds of temperature. An increase in the deposition rate increases the mole ratio. This is because at the fixed current density the increase in the deposit mass indicates the current used for the generation of dopant heavier than the pyrrole molecule. In Fig. 8, the mole ratios for P-T and PA are linearly proportional to the deposition rate. For $(mF/(tIm_a))^2 \ll 1$, Eq. (4) can approximately be

rewritten as

$$x/n \approx (m/t) (2 - m_n/m_n) F / I m_n - m_n/m_n. \quad (10)$$

According to Eq. (10), the ratio x/n becomes linearly proportional to the deposition rate m/t [15, 23-24].

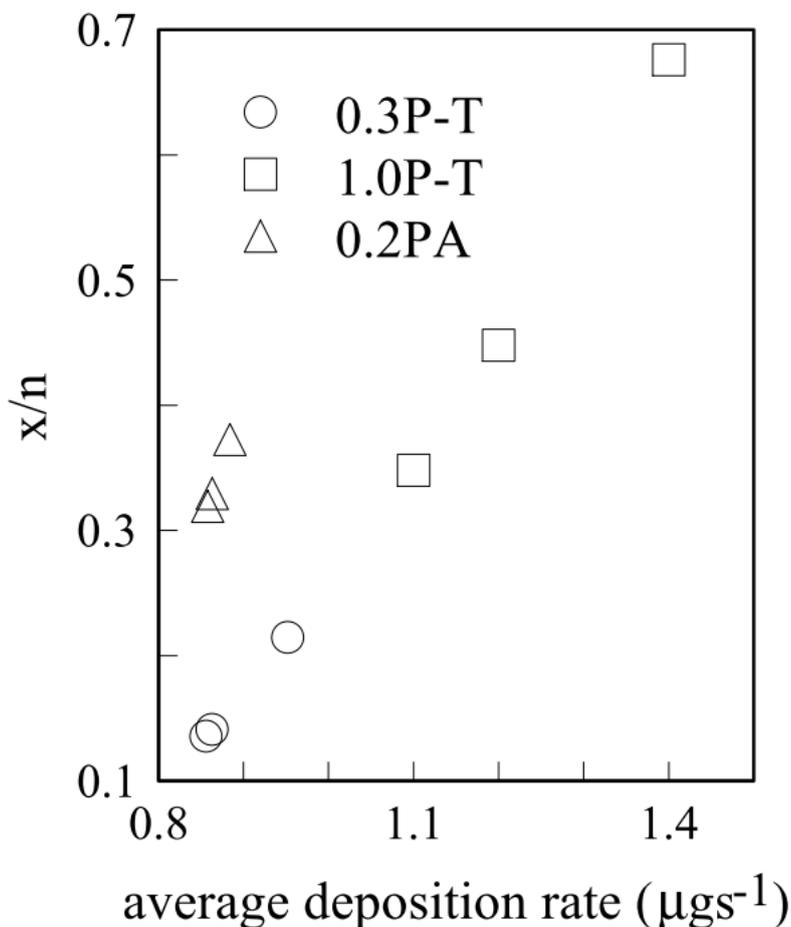


Figure 8. Dependence of the mole ratio, x/n on the average deposition rate. The ratio x/n is determined by Eq. (4) using the deposition rate in Figs. 4 and 5.

This is because the current is fixed and the charge transfer reaction for electropolymerization is dominant. Thus, we can investigate the physical property of doped pyrrole films using the mole ratio instead of the feeding content of doping agent.

3.4 Dependence of electric conductivity on the mole ratio x/n

The mechanism of electric conductivity of polypyrrole has been extensively examined [25]. A polaron generated by oxidation of polypyrrole is the charge carrier entity. The polaron from which one more electron is removed is called a bipolaron without spin. The energy of the polaron lies in an energy band close to the valence band. The population of the charge carrier entity is thermally controlled and the conducting behavior of polypyrrole is known to be typical of semiconductor.

However, polyaniline was lately reported to have a metallic conductivity using a new oxidation method [26], i.e., the transport property of the polyaniline film exhibits the same conducting behavior as that of conventional metals. The conducting property of polymers is far from complete understanding.

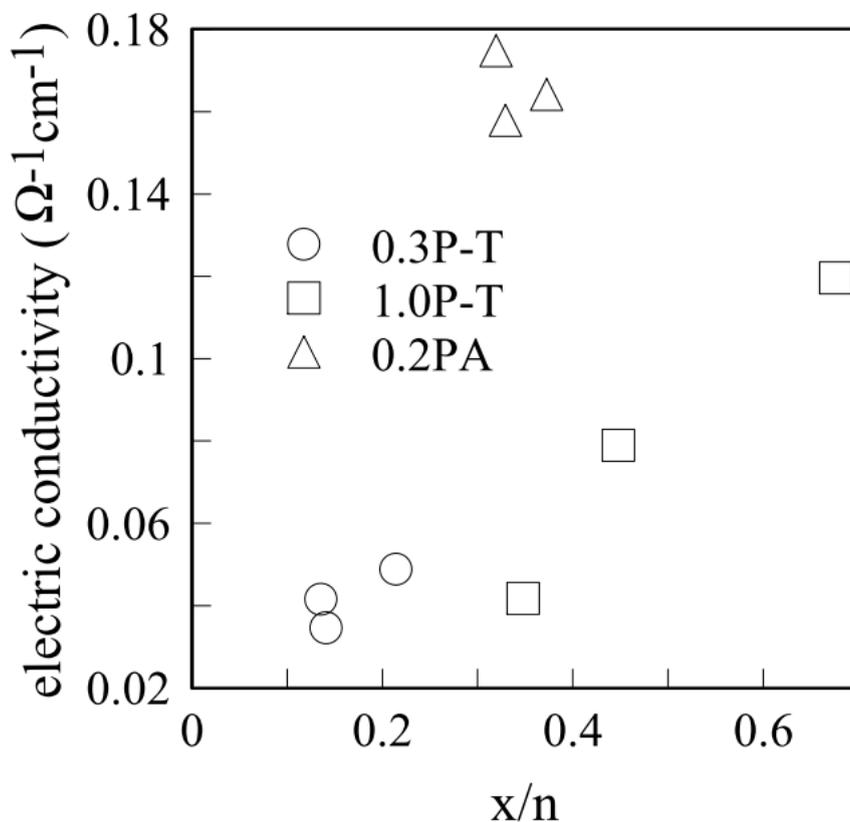


Figure 9. A plot of electric conductivity of the polypyrrole film vs. mole ratio x/n . The solid straight line is drawn to help viewing.

In Fig. 9, the electrical conductivity of the doped polypyrrole films measured by the four-point probe technique at room temperature is shown. Polypyrrole films doped with P-T and PA have been reported to have the electric conductivity ranging from 10^{-3} to $10 \Omega^{-1} \text{ cm}^{-1}$ [8, 10, 27, 28]. The electric conductivity of the polypyrrole in this experiment is within the range. In order to obtain the polypyrrole film with higher electric conductivity, more crystalline, better oriented, and defect free polypyrrole films [27-28] are required.

The electric conductivity of polypyrrole is dependent on the type of dopant agent. The change in the electric conductivity due to the type of dopant agent is thought to be caused by the interaction of a polypyrrole unit with the all its neighbors including the dopant agent [29-30]. Within the framework of band theory, the carrier, polaron is a radical ion associated with a lattice distortion and forms the localized electronic state in the band gap. The electronic state changes with the type of dopant agent but the effect is so complicated that it has not been made clear. From a macroscopic point of view, the

crystalline structure, polymerization degree, molecular orientation, and defects, which are dependent on synthesis conditions, also affect the electric conductivity.

The electric conductivity of the polypyrrole film electropolymerized from the solution including PA is distributed in a small region because of the ratio x/n almost independent of temperature. However, the electric conductivity of the polypyrrole film electropolymerized from the solution including P-T linearly increases with the mole ratio x/n . In other words, the electric conductivity is linearly proportional to the deposition rate. This indicates that the population of the charge carrier increases with the content of P-T. The mole ratio determined using the mass measurement based on the two electrochemical reactions can be related to the electric conductivity.

4. CONCLUSIONS

The grain growth of the polypyrrole film is found to obey the scaling law characterized by $z=1.61$, $\alpha=1.0$, and $\beta=0.65$ in the temperature range of 275 to 291 K. The value of β greater than 0.5 suggests that the pyrrole molecular moves in a local range of the grain-size as the local effect. The simple determination method for the mole ratio of the doping agent to pyrrole in the polypyrrole film grown at the fixed current is proposed. Using the method based on the deposit mass measurement of the polypyrrole film, the value of the mole ratio is distributed in a range of 0.13 to 0.67. The mole ratio and the electric conductivity of the P-T doped pyrrole film are shown to be linearly proportional to the deposition rate.

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