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Novel Electrochemical Phenomena in Magnetic Fields*

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Recent two topics are given of electrochemical studies in steady magnetic fields at the High Field Laboratory of Tohoku University. One is the magnetic-field-induced diffusion-limited-aggregation in the pattern formation of silver electrodeposits. The other is the magnetic field effect on the learning effect in a dopant-exchange process of an organic conducting polymer polypyrrole.

KEYWORDS: magnetic-field-induced DLA, MHD effect, polypyrrole, learning effect, diamagnetic orientation

1. Introduction

Introducing an additional field to an electrode surface develops new technique to control electrode reaction processes which may be hardly regulated by the conventional electrochemical energy. A magnetic field brings about the Zeeman effect on radicals, orientation of polymers[1] and the magnetohydrodynamic (MHD) effect[2,3]. Thus, the magneto-electrochemical technique can be expected to control the charge transfer process, the mass transport process and the morphology of electrodeposits.

In the first part of this paper we report the MHD effect on the pattern formation of the silver electrodeposits and a novel phenomenon of the diffusion-limited-aggregation (DLA) induced by the magnetic field[4]. In the second part we report the effect of diamagnetic orientation on the redox (reduction-oxidation) behavior of a polypyrrole (PPy) film electrochemically polymerized with and without magnetic field and show that the magnetic field is able to control the learning effect of the PPy film[5], which is expected to be a new application of the magnetic field to the development of an intelligent molecular device.

2. Magnetic-field-induced DLA

Fractal pattern formation in nature has been one of the most fascinating subjects in natural sciences in the past decade. A rate-determining step in pattern formation of aggregates has been proven to be significant by the studies of the DLA model[6,7] and its related computer simulations[8,9]. Electrodeposition of a metal is a good experimental system for the study of the aggregation pattern[10], exhibiting several characteristic patterns (random-fractal, dendritic, dense-radial, etc.)[11,12]. In electrolysis under magnetic fields the Lorentz force induces lateral drifts in the diffusive motion of ions, and the MHD effect brings about convection in the electrolytic cell[2,3], and hence is expected to change the morphology of the electrodeposits[13]. Here we show that the magnetic field changes the rate-determining step in the silver electrodeposition from the kinetic process to the diffusion one, resulting in the morphology change from the dendritic pattern to the random fractal one.

The electrolytic cell consisted of two glass plates with a spacer (0.3 mm thickness) and three electrodes (Fig. 1(a)); a working electrode of a carbon rod (ϕ 2 mm), a counter electrode of a silver ring and a reference electrode of Ag/Ag^+ (0.02 M (M = mol dm^{-3})). The electrodeposition was performed using a potentiostat at a constant applied potential of -0.2 V (vs. Ag/Ag^+) in a 0.1 M $AgNO_3$ aqueous solution containing 0.5 M $NaNO_3$ as a supporting electrolyte. Under such a condition the electrodeposit grew in a dendritic pattern. The ac impedance was measured during the electrodeposition by means of the noise-FFT method with a superimposed ac voltage of 10 mV (peak-to-peak) over a frequency range from 1 Hz to 1 kHz.

The magnetic field was applied perpendicularly to the glass plates during the electrodeposition with a large-bore (ϕ220 mm) superconducting magnet (Fig. 1(b)), causing the MHD convection around the working electrode. The temperature within the magnet was controlled at 25 ± 0.1 °C

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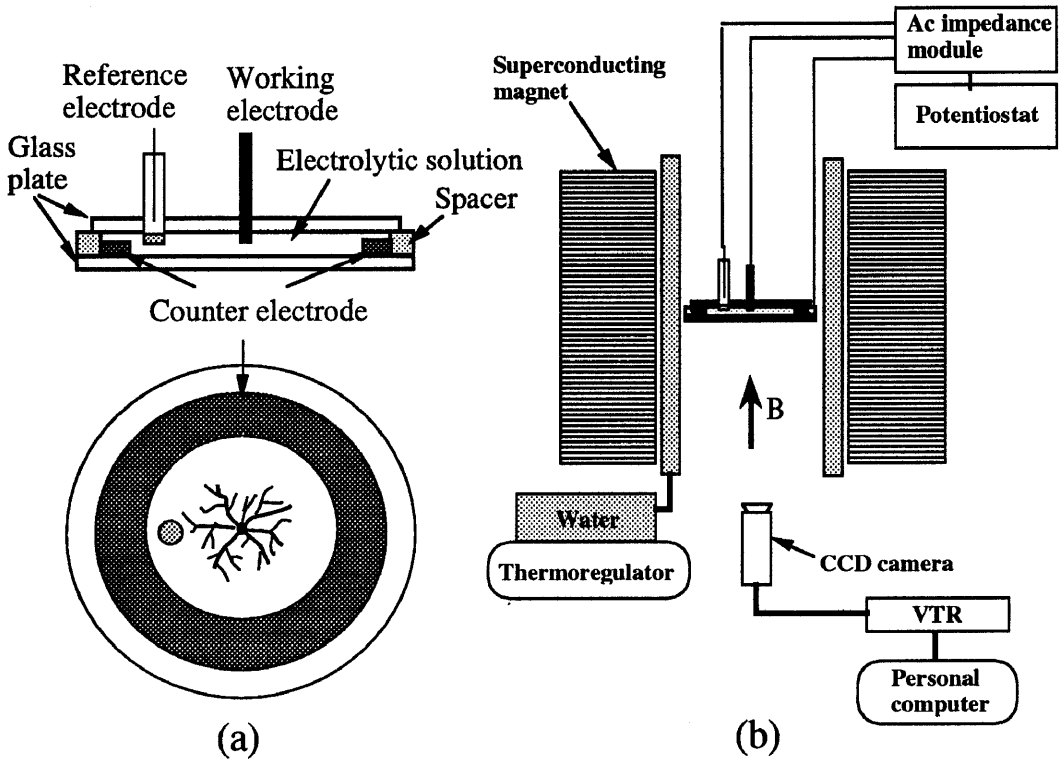

Figure 1. Schematics of (a) the electrolytic cell and (b) the observation of the growth patterns in magnetic fields B.

by a water-circulating thermoregulator. The growth patterns were observed using a CCD camera and recorded on a videorecorder. The image data were transferred to a personal computer and digitized. The fractal dimension of the patterns was estimated by the box-counting method.

The growth patterns of the silver electrodeposits in the magnetic fields are shown in Fig. 2. The dendritic pattern in 0 T (Fig. 2(a)) changes into the asymmetric dendrite, in which side branches develop on the upstream side of main branches (Fig. 2(b)). In the higher magnetic fields of 0.3 and 0.5 T, the growth pattern drastically changes into random fractal patterns (Figs. 2(c) and 2(d)), suggesting the DLA growth. In addition, a spiral growth toward the upstream is seen in the pattern for 0.5 T.

We measured the current during the electrodeposition and found that it decreased with increasing magnetic field; the averaged current was approximately 1 mA in 0 T and 0.4 mA in 0.5 T. This result indicates that the magnetic field reduced the growth rate of the electrodeposit.

In order to examine the rate-determining step we measured the *in situ* ac impedance during the electrodeposition. The frequency dispersion of the complex impedance $Z = Z' + iZ''$ is shown in Fig. 3 by the Cole-Cole plot of $-Z''$ vs. Z'. It is well known that the Cole-Cole plot shows a straight line with the slope $\Delta = 1$ in the diffusion-limited process and a

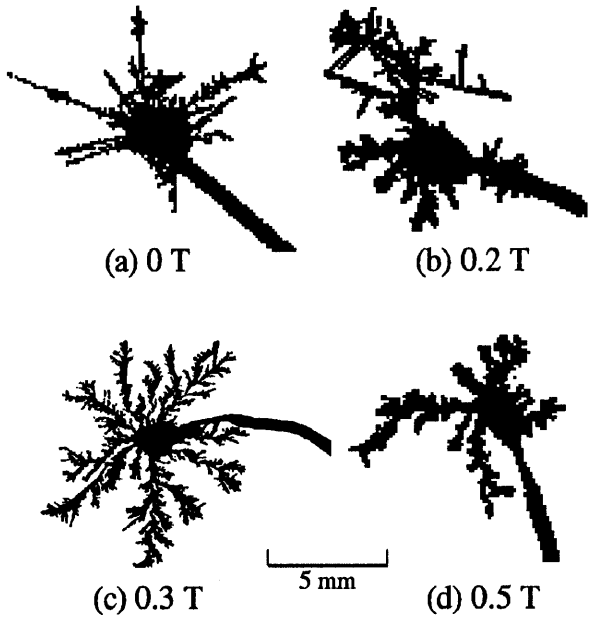

Figure 2. Growth patterns of the silver electrodeposits in magnetic fields of (a) 0 T; (b) 0.2 T; (c) 0.3 T; and (d) 0.5 T. The electrodeposition was performed at a constant applied potential of -0.2 V (vs. Ag/Ag^+) in a 0.1 M $AgNO_3$ aqueous solution containing 0.5 M $NaNO_3$ as a supporting electrolyte. The magnetic field was applied perpendicularly to the glass plates (from the front to the back in the figures), causing the clockwise MHD convection around the working electrode.

semicircle in the kinetic-controlled process[14,15]. The frequency dispersion in 0 T has the form of a depressed semicircle (Fig. 3(a)), while the dispersion in 0.5 T is on a nearly straight line with $\Delta = 1$ below 30 Hz (Fig. 3(b)). A similar straight-line dispersion was also observed in 0.3 T. These results indicate that the electrodeposition is kinetic-controlled in 0 T and diffusion-limited in 0.3 and 0.5 T, and the magnetic field thus changes the rate-determining step from the kinetic process to the diffusion one.

The computer simulations of DLA and the dendritic growth demonstrated that the aggregate changes from the random fractal pattern into the dendritic one with increasing probability of the surface diffusion[8,9], where the particles diffuse on a growing interface and then stick on kinks or steps. The kinetic-controlled process in the dendritic growth in 0 T is hence considered to include the surface-diffusion process.

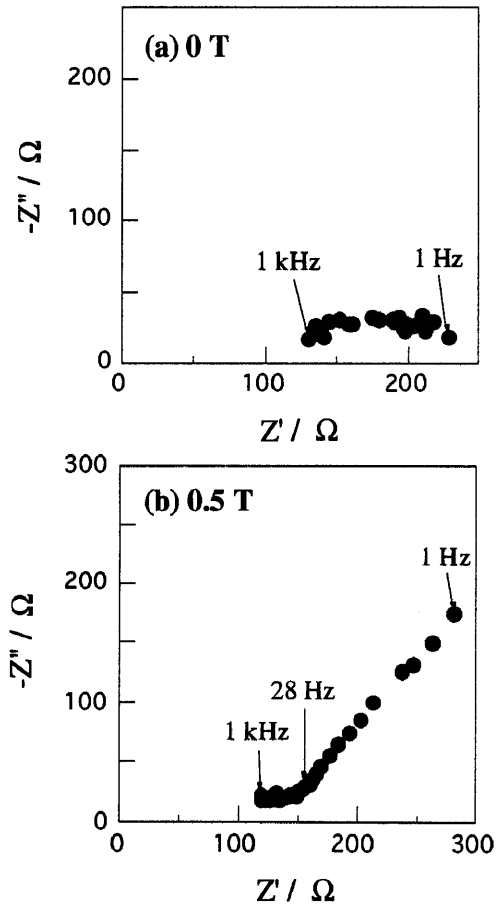

Figure 3. Frequency dispersion of the *in situ* ac impedance during the silver electrodeposition in (a) 0 T and (b) 0.5 T. The dispersion of the complex impedance $Z = Z' + iZ''$ is shown by the Cole-Cole plot of $-Z''$ vs. Z'. The ac impedance was measured at the constant potential of -0.2 V (vs. Ag/Ag^+) with a superimposed ac voltage of 10 mV (peak-to-peak) over a frequency range from 1 Hz to 1 kHz.

The depressed semicircle in Fig. 3(a) might arise from the geometrical inhomogeneity of the reaction surface[16]. The asymmetric dendrite in 0.2 T reflects the higher arrival probability on the upstream side of the main branches owing to the MHD convection. On the other hand, the growth patterns in 0.3 and 0.5 T are random fractal ones which resemble the DLA form[6,7]. The fractal dimension of the pattern in 0.3 T was estimated to be 1.73, in good agreement with that of the DLA model simulation[7]. The frequency dispersions in 0.3 and 0.5 T show that the random fractal growth can be electrochemically regarded as the diffusion-limited process.

Saito *et al.* studied the effect of a lateral drift on the morphology of the dendritic growth by the Monte Carlo simulation of the lattice-gas model[17]. They showed that the lateral drift brings about the asymmetric dendrite with the development of the side branches on the upstream side, as observed in our result (see Fig. 2(b)). However, such a drift never changes the dendritic pattern into the DLA-like one.

It is generally likely that the MHD convection makes the diffusion layer thinner, hence causing a compact pattern of the electrodeposits[13]. Here an intriguing question has been raised as to why the magnetic field brings about DLA in the present results. There are two possible answers to this question; one is that the magnetic field accelerates the kinetic process, and the other is that it decelerates the diffusion process. The fact that the averaged current during the electrodeposition decreases with increasing magnetic field indicates the latter case. We thus considered that the lateral drift of the Lorentz force reduces the apparent diffusion rate of the ions, leading to DLA.

In conclusion, we have found a new phenomenon, "magnetic-field-induced DLA", in electrodeposition. The pattern formation in magnetic fields is of great potential interest in the studies of aggregating patterns in external fields, which occur over a wide range of length scales from nanocrystal growth to galactic systems in the universe.

3. Control of the lerning effect of polypyrrole by magnetic fields

Organic conducting polymers are of great potential interest in connection with a neural element because they exhibit fractal growth[18,19], the learning effect[20] and the electrical plasticity[21,22]. Iseki *et al.* reported that a p-toluenesulfonate-doped polypyrrole (PPy/TsO^-) film shows electrically plastic behavior (or the learning effect), which

is gradual activation of the film in a dopant-exchange (DE) process during redox cycles in electrolytic solutions containing spherical anions (e.g. NO_3^-, ClO_4^- and BF_4^-)[22]. The PPy/TsO^- film has an anisotropic molecular organization, where the planes of aromatic rings lie preferentially parallel to the electrode surface, while the spherical-anion-doped PPy film has an isotropic organization[23,24]. The DE process between TsO^- and the spherical anions is thus considered to cause the considerable change in the film morphology[25]. On the other hand, it is well known that most organic polymers have so large anisotropy in a diamagnetic susceptibility that they are subject to the diamagnetic orientation, resulting in the morphological changes, in magnetic fields[1]. Considering these facts, we have tried to control the learning effect in the DE process of the PPy/TsO^- film by the magnetic field.

The electrochemical measurements were performed at 20 °C with an electrochemical analyzer BAS-100B/W. The electrode system consisted of a platinum disk (φ1.6 mm) as a working electrode, a Ag/AgCl electrode as a reference one and a platinum plate as a counter electrode. The PPy/TsO^- film was prepared on the platinum disk electrode by electrochemical polymerization[26] (1.0 C cm^{-2}) at a constant potential (1.0 V) in a 0.1 M pyrrole aqueous solution containing 0.1 M TsONa as a supporting electrolyte. In order to examine the learning effect of the DE process, we measured the cyclic voltammogram (CV) of this film in a 0.1 M $LiClO_4$ aqueous solution in a potential range of -0.5 ~ 0.5 V, where gradual current increase is clearly observed with repeating redox cycle. The undoping process in the PPy/TsO^- film occurs at -0.5 ~ -0.6 V[25], hence the more negative potential sweep leads to rapid saturation of the current within 10 cycles. On the other hand, the repeating potential sweep of -0.3 ~ 0.5 V results in only slight current increase caused by the spontaneous DE process. The CV's were measured just after the immersion of the film in the $LiClO_4$ solution to eliminate the influence of the spontaneous DE process.

The magnetic field generated by a Bitter magnet was applied perpendicularly to the surface of the working electrode and parallel to the faradaic current to eliminate the magnetohydrodynamic effect as described[27].

We set out to investigate the magnetic field effect on the DE process of the PPy/TsO^- film prepared in the absence of magnetic field. Figure 4 shows the CV's (30 cycles) of the

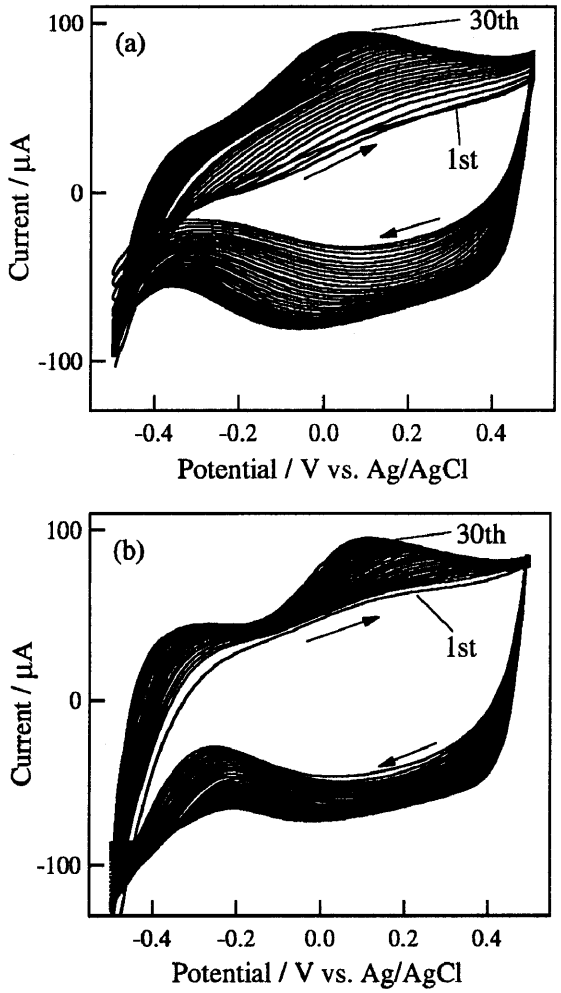

Figure 4. Cyclic voltammograms (CV's) of the PPy/TsO^- film measured in (a) 0 T and (b) 12 T. The film was prepared in 0 T. The CV's were measured for 30 cycles in a 0.1 M $LiClO_4$ aqueous solution after keeping the potential at -0.5 V for 2 s. The potential sweep rate was 50 mV s^{-1}, and arrows represent the sweep direction.

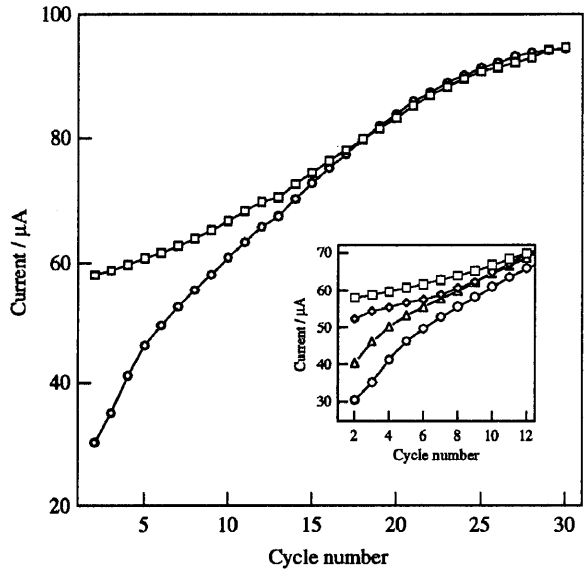

Figure 5. Plots of the doping (anodic) current at 0.084 V in 0 T (circle) and 12 T (square) as a function of the cycle number in the CV's in Fig. 4. The inset shows similar plots for the first 12 cycles in 0 T (circle), 1 T (triangle), 6 T (rhombus) and 12 T (square).

film measured in (a) 0 T and (b) 12 T. Both doping (anodic) and undoping (cathodic) currents increase with repeating potential sweep, and the PPy film undergoes the doping and undoping processes of ClO_4^- instead of TsO^-. Figure 5 shows the plots of the anodic current at 0.084 V in the CV's in 0 T and 12 T as a function of the cycle number. It is clearly seen that the magnetic field increases the doping current at the initial stages of the DE process (in the first 15 cycles), and such an effect is enhanced with increasing magnetic field (see the inset in Fig. 5). This result indicates that the magnetic field facilitates the morphological changes of the PPy film and accelerates the DE process.

As mentioned above, in the PPy/TsO^- film the planes of aromatic rings lie preferentially parallel to the electrode surface and the dopant molecules lie between the PPy layers[24].

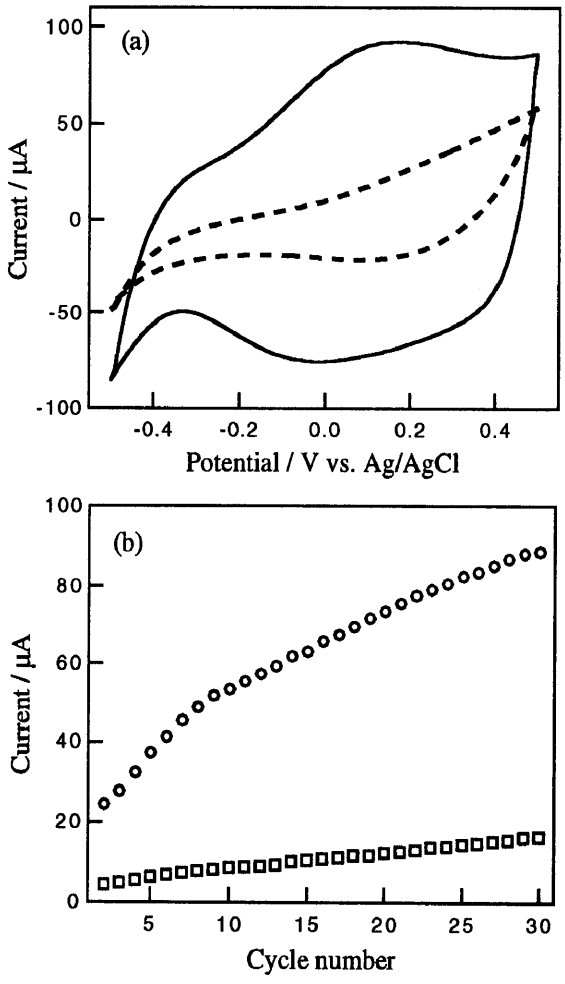

Figure 6. (a) Cyclic voltammograms (the 30th cycle) of the PPy/TsO^- films prepared in 0 T (solid) and 12 T (dotted). The CV's were measured in 0 T with the potential sweep rate of 50 mV s^{-1} in a 0.1 M $LiClO_4$ aqueous solution after keeping the potential at -0.5 V for 2 s. (b) Plots of the doping (anodic) current at 0.084 V of the PPy/TsO^- films prepared in 0 T (circle) and in 12 T (square) as a function of the cycle number.

On the other hand, the aromatic ring is most stable at the orientation parallel to the magnetic field because of the large diamagnetic susceptibility perpendicular to the ring plate[1]. In the present experiment the magnetic field is applied perpendicularly to the electrode surface, it is thus speculated that the magnetic field degrades the anisotropic organization of the PPy/TsO^- film, resulting in the acceleration of the DE process.

Our previous paper[28] showed that the magnetic field induces the oriented polymerization of pyrrole owing to the diamagnetic effect, resulting in the drastic morphological change from an open-ramified fractal pattern in 0 T to a closed pattern in 0.5 T. We examined the DE process of the PPy/TsO^- film prepared in the magnetic field of 12 T. The CV's (the 30th cycle) of the films prepared with and without magnetic fields are shown in Fig. 6(a), where the CV's were measured in the absence of magnetic field. Figure 6(b) shows the plots of the doping current at 0.084 V in both CV's as a function of the cycle number. It is obviously seen that the PPy/TsO^- film prepared in 12 T shows only slight current increase, being considered to be so rigid that the dopant anions cannot migrate within the film. Such suppression of the plastic behavior was observed in the PPy/TsO^- film prepared in the magnetic fields higher than 1 T.

In summary, we have shown two opposite effects of the magnetic field on the DE process in the PPy/TsO^- film; one is the acceleration, and the other is the suppression. Both effects seem to arise from the diamagnetic orientation of the aromatic rings, but the detailed mechanism is a future subject. The feasibility of such control of the learning effect is essential for the development of an intelligent molecular device.

Acknowledgements

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