© *1997 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***70***, *2337—2340 (1997)*

Magnetic-Field-Induced Deactivation of Polypyrrole Films in Repeated Redox Cycles

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(Received April 30, 1997)

Magnetic field effects on the durability of anion-doped polypyrrole (PPy/anion) films were studied by measuring successive cyclic voltammograms in a cryocooler-cooled superconducting magnet. The deactivation, which means positive shifts of the anodic peak potential, was observed in PPy/ClO_4^- and PPy/Cl^- films under the magnetic fields of 2 and 5 T. This magnetic-field-induced deactivation has a novel aspect that is an accumulative effect of the magnetic fields. On the other hand, the degradation of PPy/*p*-toluenesulfonate films, which means a current decrease in the voltammograms, was not affected by the magnetic field of 5 T.

Recent development of a cryocooler-cooled superconducting magnet,[1] which is easily handled without liquid helium, has stimulated us to explore new phenomena in high magnetic fields. We have made attempts at the "magneto-electropolymerization" (electropolymerization in magnetic fields) of pyrrole and reported that the magnetic fields bring about drastic changes in the growth morphology and redox behavior of polypyrrole (PPy).[2—4] Such magnetic field effects on the electropolymerization are considered to come from the diamagnetic orientation of the polymer. Most organic polymers have such a large anisotropy in diamagnetic susceptibility that they are subject to the diamagnetic orientation, resulting in morphological changes, in magnetic fields.[5—8]

Oxidation and reduction of conducting polymers such as PPy and polythiophene accompany doping and undoping of anions, respectively, and hence lead to morphological and volume changes of the polymers during a redox cycle.[9,10] Harada et al. studied the durability of polythiophene films during repeated redox cycles and found the deactivation and the degradation of the films.[11] The former is indicated by a positive shift of the anodic peak in the cyclic voltammogram (CV) and the latter by a current decrease of the CV. Magnetic fields are expected to affect the morphological changes of polymer films during the redox cycles through the diamagnetic orientation.[12] We have tried to examine the repeated redox behavior of PPy films in magnetic fields and found a new phenomenon of the magnetic field-induced deactivation.

Experimental

All chemicals were of guaranteed reagent grade. The electrochemical measurements were done using Solartron SI-1208B. The electrode system consisted of a platinum disk (ϕ 1.6 mm) as a working electrode, an Ag/AgCl electrode as a reference one, and a platinum plate as a counter electrode. The PPy films were prepared on the platinum disk electrode by oxidative electropolymerization, which produces the anion X^- doped polypyrrole (PPy/X^-). The electropolymerization was carried out in the absence of a magnetic field by passing the charge of 1.0 C cm^{-2} at a constant potential (1.0 V) in a 0.1 M (1 M = 1 mol dm^{-3}) pyrrole aqueous solution containing 0.1 M supporting electrolytes ($NaClO_4$, $LiClO_4$, Et_4NClO_4, NaCl, and TsONa (sodium *p*-toluenesulfonate)). The CV's of the PPy/X^- ($X^- = ClO_4^-, Cl^-, TsO^-$) films were measured with a potential sweep rate of 50 mV s^{-1} in the aqueous solution containing the same supporting electrolyte as used at the electropolymerization. The a.c. impedance of the film was measured by means of the single sine correlation method over a frequency range from 0.1 Hz to 20 kHz with the ac voltage of 10 mV.

The magnetic fields were generated by a cryocooler-cooled superconducting magnet,[1] which can produce up to 5.5 T in a 220 mm room-temperature bore. The electrochemical cell was placed at the center of the magnet, and the temperature within the magnet was controlled at 20 ± 0.1 °C by using a water-circulating thermoregulator. The magnetic fields were applied perpendicularly to the surface of the working electrode and parallel to the faradaic current to eliminate the magnetohydrodynamic effect[13]. The schematic diagram of the experimental setup was described elsewhere.[12]

Results and Discussion

Deactivation of PPy/ClO_4^- and PPy/Cl^-. To examine the durability of the PPy films we measured the CV's for 100 cycles in a potential range from 0.5 to −0.5 V with and without the magnetic fields. Figure 1 shows the CV's (the 10th, 80th, and 100th cycles) of the PPy/ClO_4^- film in a 0.1 M $NaClO_4$ aqueous solution under (a) zero field and (b) 5 T. While no considerable change was seen in the CV's at 0 T, a remarkable positive shift of the anodic peak is seen in the CV's at 5 T. The anodic peak potentials E_{pa} of the CV's at 0 T, 2 T, and 5 T are plotted as a function of the cycle number in Fig. 2. No remarkable difference among them is seen in the first 30 cycles. The magnetic field effect appears around the 40th cycle, and then the peak potential difference with and without the magnetic fields increases with increasing the

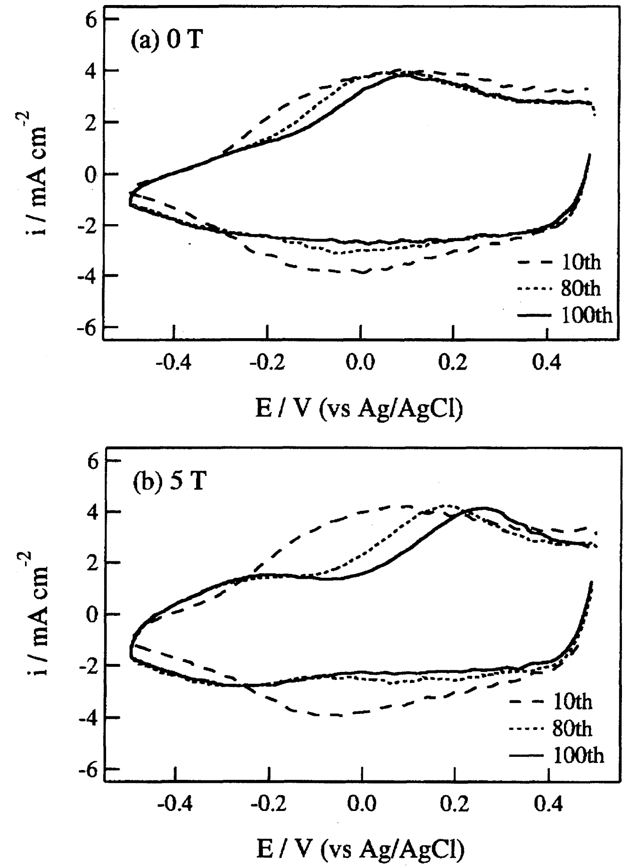

Fig. 1. Successive cyclic voltammograms (the 10th, 80th, and 100th cycles) of the PPy/ClO_4^- film in a 0.1 M $NaClO_4$ aqueous solution under (a) 0 and (b) 5 T.

cycle number and the magnetic field.

We examined the ac impedance of the PPy/ClO_4^- film at 0 V under zero magnetic field after the redox cycles in the 0.1 M $NaClO_4$ aqueous solution. Figure 3 shows the Cole–Cole plots of the frequency dispersion of the complex impedance $Z=Z'+jZ''$ $(j=\sqrt{-1})$. The dispersion curves **a** and **b** were measured after the 100 cycles in 0 and 5 T, respectively. The frequency dispersions have a semicircle, whose diameter corresponds to the reaction resistance. It is found that the reaction resistance of the curve **b** is approximately two times larger than that of the curve **a**. This result is consistent with the positive shift of the anodic peak of the CV's in 5 T.

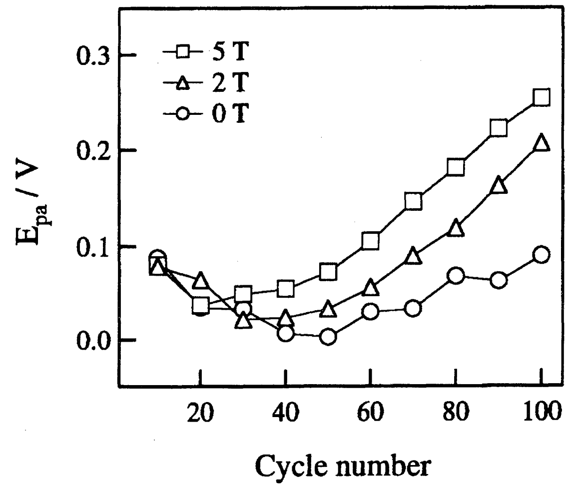

Fig. 2. Shifts of the anodic peak potentials in the CV's of the PPy/ClO_4^- film in a 0.1 M $NaClO_4$ aqueous solution under 0, 2, and 5 T.

As mentioned above, the positive shift of the anodic peak was found in the repeated CV's of polythiophene films in the absence of a magnetic field and is called "deactivation". Harada et al.[11] demonstrated that the deactivated film could be reactivated by polarizing at a highly positive potential. Such results mean that the deactivation arises from the accumulation of cations trapped within the film during the repeated redox cycles.

In the present case, the deactivation is induced by the magnetic fields. In order to reactivate the film we measured the CV in the higher potential range from 1.0 to −0.5 V after the 100 cycles CV's in 5 T. The result is the curve of the 101st cycle in Fig. 4, in which the 100th CV is drawn for the comparison. The anodic peak of the 101st CV appears around 0.1 V, indicating that the deactivated film is reactivated by the highly positive polarization. The a.c. impedance of the

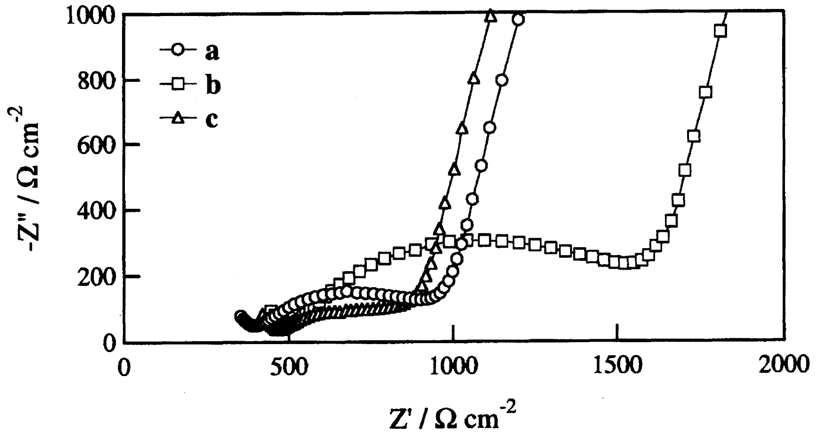

Fig. 3. Frequency dispersions of the ac impedances of the PPy/ClO_4^- film after 100 redox cycles in **a** 0 and **b** 5 T. The dispersion curve **c** was measured after 101st cycle in Fig. 4. The a.c. impedances were measured in a 0.1 M $NaClO_4$ aqueous solution under zero magnetic field.

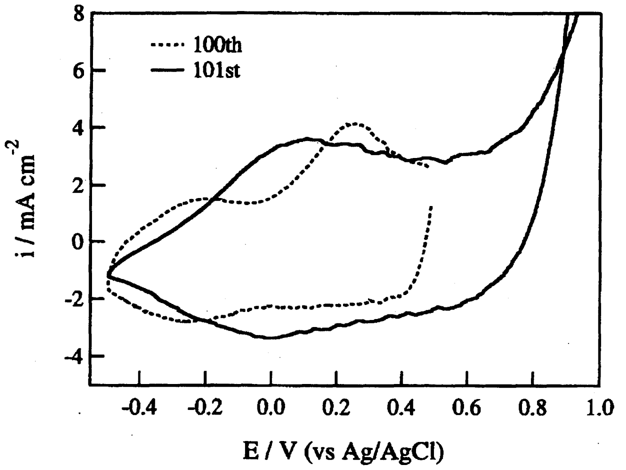

Fig. 4. Successive cyclic voltammograms (the 100th and 101st cycles) of the PPy/ClO_4^- film in a 0.1 M $NaClO_4$ aqueous solution under 5 T. The 101st cycle was measured in a potential range from 1.0 to −0.5 V to reactivate the film.

reactivated film was measured after the 101st CV in the same solution, and the frequency dispersion is shown in Fig. 3 (the curve **c**). The reaction resistance is drastically decreased by the positive polarization. These results show that the magnetic-field-induced (MFI) deactivation also arises from the accumulation of trapped cations.

To examine the effect of the cation size on the MFI deactivation, the CV's of the PPy/ClO_4^- film were measured in 0.1 M $LiClO_4$ and Et_4NClO_4 aqueous solutions with and without the magnetic field. The MFI deactivation was observed in both solutions, and the anodic peak shifts are shown in Fig. 5. Comparing the results of Figs. 2 and 5, it is found that the MFI deactivation is insensitive to the cation sizes. This result is quite different from the case of polythiophene without a magnetic field in Ref. 11, in which the bulky quaternary ammonium cations deactivate the films and the alkali cations do not.

The MFI deactivation was also observed in the PPy/Cl^- film as shown in Fig. 6, which shows the plots of anodic peak potential of the CV's in a 0.1 M NaCl aqueous solution. The peak potential difference between 0 and 5 T is obviously smaller than that of the PPy/ClO_4^- films, implying that the MFI deactivation depends on the dopant anion size.

Here we consider the mechanism of the MFI deactivation. The oxidation of PPy accompanies the doping of anions for the charge compensation of the film. The successive reduction process accompanies the undoping of anions or the doping of cations. If some of the cations are left in the film at the next oxidation process, the cations are accumulated in the film during the successive redox cycles. The fact that the highly positive polarization reactivates the film (Fig. 4) indicates that the MFI deactivation is caused by the accumulation of cations trapped within the film. Why do the magnetic fields induce the trapping of cations during the repeated redox cycles? The film changes its morphology and volume in the doping–undoping processes.[9,10] The motion of the aromatic molecular chains is affected by the magnetic field through the diamagnetic orientation.[5,8] It is presumed that the magnetic field changes the alignment of the molecular chains during the doping–undoping processes, and thereby the film mor-

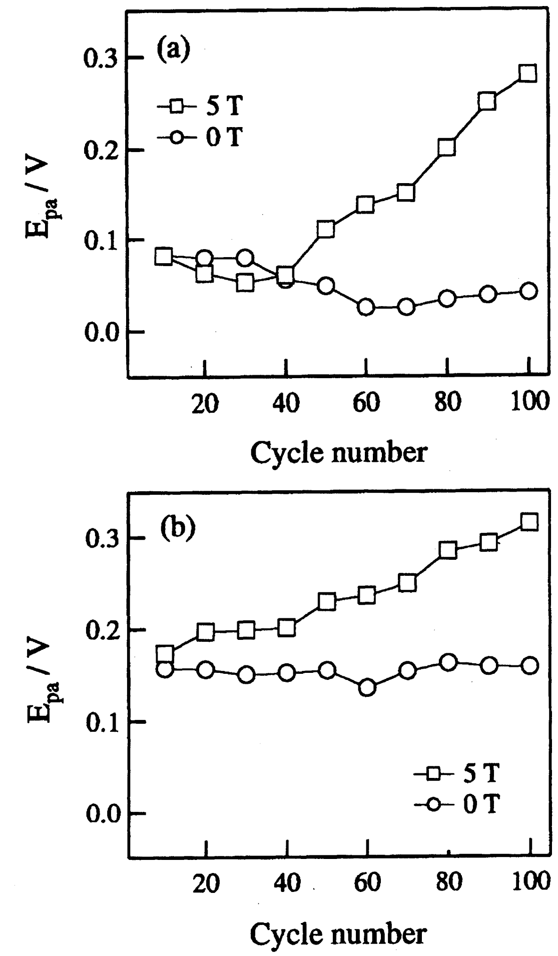

Fig. 5. Shifts of the anodic peak potentials in the CV's of the PPy/ClO_4^- film in 0.1 M (a) $LiClO_4$ and (b) Et_4NClO_4 aqueous solutions under 0 and 5 T.

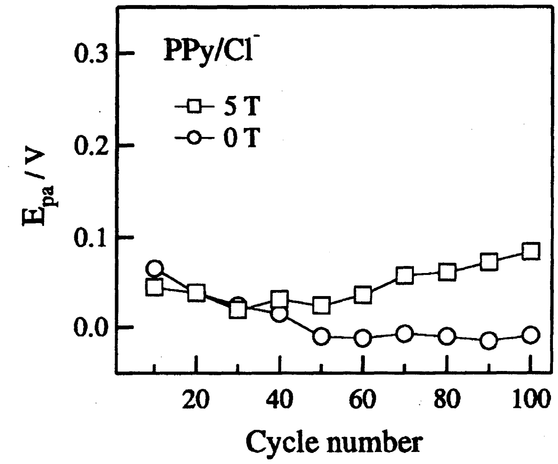

Fig. 6. Shifts of the anodic peak potentials in the CV's of the PPy/Cl^- film in a 0.1 M NaCl aqueous solution under 0 and 5 T.

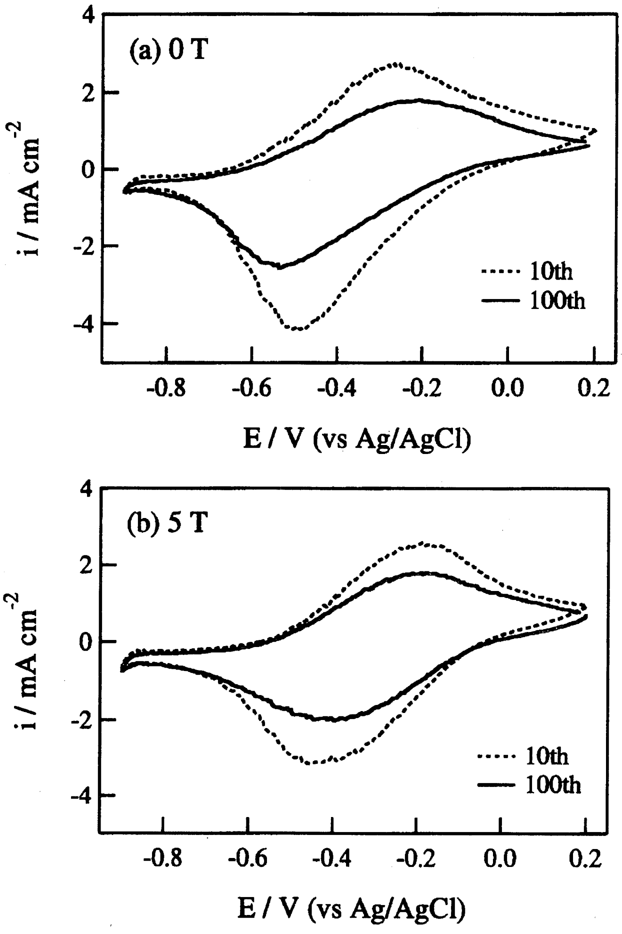

Fig. 7. Successive cyclic voltammograms (the 10th and 100th cycles) of the PPy/TsO$^-$ film in a 0.1 M TsONa aqueous solution under (a) 0 and (b) 5 T.

phology becomes different from that in zero magnetic field. Although such a morphological change would be slight in one redox cycle, it is accumulated during the repeated cycles, affecting the mobility of dopants. Actually, the MFI deactivation in the PPy films appears clearly after the 40th cycle (see Figs. 2, 5, and 6).

Our experimental results show that the anodic peak shift of the PPy/ClO$_4$$^-$ film is larger than that of the PPy/Cl$^-$ film (see Figs. 2 and 6). The doping–undoping of a larger anion accompanies the larger motion of the PPy chains, leading to the larger MFI deactivation. On the other hand, there remains a question why the MFI deactivation is insensitive to the cation size (Figs. 2 and 5).

Degradation of PPy/TsO$^-$. The durability of the PPy/TsO$^-$ film was investigated in a 0.1 M TsONa aqueous solution, and the CV's of the 10th and 100th cycles are shown in Fig. 7. Both successive CV's in 0 and 5 T exhibit similar behavior. While a remarkable shift of the peak potential is not seen during the repeated cycles, the redox peak currents at both 0 and 5 T obviously decrease with increasing cycle number.

The current decrease during the successive CV's was also found in the polythiophene films, and was called "degradation".[11] The degradation is caused by a nucleophilic attack of anions on the oxidized state of the polymer backbone. If the degradation of the PPy/TsO$^-$ film comes from the same mechanism, the TsO$^-$ ions would attack on the PPy backbones. Because such a chemical reaction occurs in a local area of the molecular scale, the degradation is not affected by the diamagnetic orientation which occurs on a more macroscopic scale.

Conclusion

We have found a novel phenomenon of MFI deactivation in the PPy/ClO$_4$$^-$ and PPy/Cl$^-$ films, which is caused by the accumulation of trapped cations within the films during the repeated redox cycles in magnetic fields. The characteristic of the MFI deactivation is the accumulative effect of magnetic fields, which will be significant not only for materials processing but for the studies of magnetic field effects on biological systems. On the other hand, the magnetic field has no influence on the degradation of the PPy/TsO$^-$ film.

We thank Professor M. Motokawa for encouraging this work and also Professor A. Konno for helpful discussions. The experiments with the magnetic fields were done in the High Field Laboratory for Superconducting Materials, Tohoku University. This work was supported in part by the Magnetic Science Project of the Japan Science and Technology Corporation, and Iron and Steel Institute of Japan.

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