Synthetic Metals, *55–57* (1993) 601–606

IN SITU ESR OF POLYANILINE BY ELECTROCHEMICAL DOPING: POLARON TO PAULI-LIKE INSTEAD OF POLARON TO BIPOLARON

K. MIZOGUCHI, T. OBANA*, S. UENO+ and K. KUME
Dept. of Physics, Tokyo Metropolitan University, Tokyo (Japan)

ABSTRACT

Polyaniline film was synthesized electrochemically with HBF_4 as an electrolyte. A potential was changed step by step to measure ESR spectra. At low doping levels ESR line shape was found to be a single Lorentzian. At higher doping levels, however, it was composed of double Lorentzians; narrow line and broad one. An integral intensity of the broad line becomes larger than that of the sharp one at the higher potentials. Temperature dependence of spin susceptibility suggested that the sharp line behaves as a Curie spin and the broad one does as a Pauli one, which is consistent with low frequency ESR result on the chemically prepared emeraldine salt with BF_4^-. The sharp line can be interpreted as a polaron created in an initial stage of the electrochemical doping. Presumable origin of the broad line was discussed.

Key Words: polyaniline, electrochemical doping, in-situ ESR, Curie-susceptibility, Pauli-susceptibility, polaron, bipolaron, Lorentzian

INTRODUCTION

In the conducting polymers polyaniline (PANI) is an interesting system because of its excellent stability in air and variety of electronic states controllable by protonation and redox process [1]. The protonation induces an electrical conductivity change more than 10 orders of magnitudes, from 10^{-10} S/cm up to several S/cm for powder samples and several hundreds S/cm for stretch-oriented films [1]. Protonated PANI (polyemeraldine salt) has been known to show Pauli-like susceptibility in chemically synthesized powders (ES-I), which is approximately proportional to the protonation level. This experimental observation has been interpreted as a characteristic behavior of

---

*Present address: Mitsui Knowledge Industry, 3-7-4 Kôji-machi, Chiyoda-ku, Tokyo, Japan
+Present address: OEC, Soft Park, 17-57 Higashi Kasuga-cho, Oita, Japan

0379-6779/93/$6.00

formation of a polaronic lattice [2] and/or percolative protonation [2,3]. A recent study of a highly crystalline film casted from N-methyl pyrrolidone (NMP) solution also showed the Pauli-like susceptibility which was not proportional to the protonation level, y, but appear suddenly around y=0.2~0.3 (ES-II). This new behavior was tried to explain by a protonation in amorphous region which produces bipolarons at small y's and a protonation in crystalline region forming a polaron lattice at large y's [4].

On the other hand, a PANI film behaved complicatedly in the electrochemical redox studies. The electron spin susceptibility has a peak as a function of redox potential, explained by a transition from polaron to bipolaron states, but at the higher potentials than the peak it was strongly dependent on a thickness of the films [5]. Thinner the film thickness, faster the decrease of susceptibility. This interesting phenomenon should include some important physics on a conduction mechanism in PANI.

In this paper, in order to investigate an evolution of electronic states when poly-leucoemeraldine salt is oxidized electrochemically [6], we will demonstrate a spin susceptibility study in an electrochemical cell as a function of potential and in dry films as a function of temperature. The result is not so simple, but showed two different signals: Curie-like susceptibility at low doping levels and Pauli-like susceptibility at high doping levels.

EXPERIMENTAL

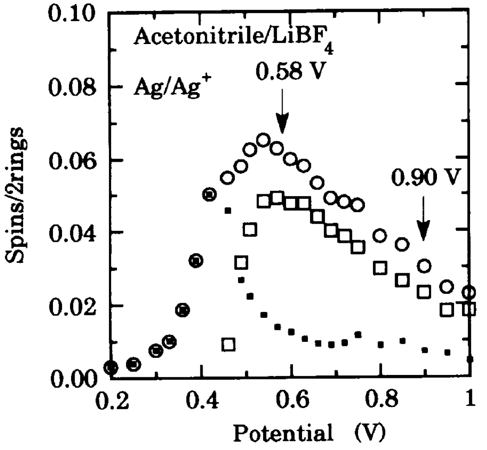
Poly-emeraldine salt films was synthesized following a reported procedure [7]. Aqueous solution of 5M HBF_4 and 0.4M Aniline distilled before synthesis was used with 0.3mmϕ Pt wire as a working electrode and Ag/AgCl as a reference electrode. Potential was swept between 0.3 and 0.6 V with 50 mV/s and a maximum current of 1~2 mA.

For *in situ* ESR measurement, an organic electrolyte of acetonitrile/2M $LiBF_4$ was used to reduce dielectric loss and Ag/Ag^+ reference electrode. The synthesized poly-emeraldine salt was transferred from the aqueous electrolyte to the organic electrolyte. ESR measurement was done under a deoxygenated atmosphere to avoid a broadening of line width by the oxygen [5,8]. ESR signal was taken after the current going to zero in each potential step of several tenth mV. An integrated intensity of ESR signal was compared with a signal of NBS Ruby standard by a double cavity at X-band (JEOL RE-3X).

For a temperature dependence study, films on Pt wire was dried and evacuated for several hours and sealed into a glass tube with helium gas for heat exchange.

RESULTS

Figure 1 indicates the room temperature spin susceptibility of PANI film with thickness of 7000 Å as a function of potential. A marked feature of this figure is a presence of two different contributions to the total spin susceptibility; the first peak around 0.4 V and the second one around 0.6 V. Both of the ESR signals are found to



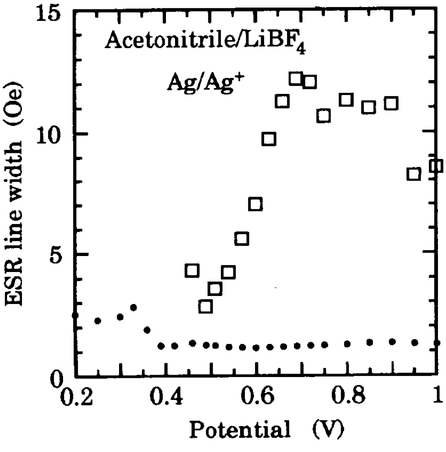


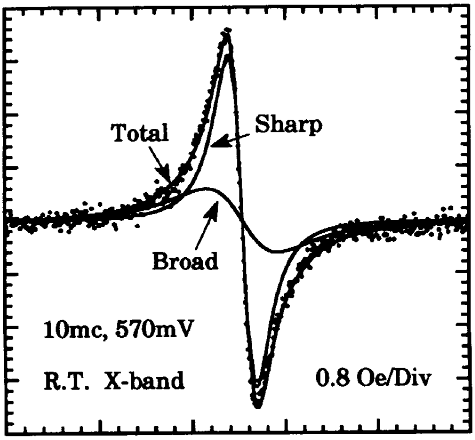
Fig. 1. (Left) The spin susceptibility of 7000 Å PANI film as a function of potential between Pt working and Ag/Ag$^+$ reference electrodes. ○ Total spin susceptibility, ■ spin susceptibility for the sharp line and □ spin susceptibility for the broad line.

Fig. 2. (Right) ESR line widths of two Lorentzians as a function of potential.

have Lorentzian line shape and almost the same g value as each other. The line width of ESR for the first peak is narrower than that for the second one as shown in Fig. 2. Typical line shape composed of two Lorentzians is shown in Fig. 3.

To investigate a nature of these signals, temperature dependences of the spin susceptibility was studied. Figure 4 shows the spin susceptibility of the dried PANI film on the Pt electrode prepared at 0.58 and 0.9 V. The observed susceptibilities can be interpreted well by a relation $\chi_{\mathrm{Obs}} = \chi_{\mathrm{P}} + \chi_{\mathrm{C}}$, where the χ_{P} is the Pauli and χ_{C} is the Curie susceptibilities, as shown by the solid and the broken lines, respectively, in Fig. 4. Here, notice an interesting relation that the intensity ratio of the broad line to the sharp one estimated from Fig. 1. is closely related to the ratio of the Pauli to the Curie susceptibility estimated at 300 K in Fig. 4. This relation implies that the broad ESR signal corresponds to the Pauli susceptibility and the sharp one does to the Curie one.

The same correspondence was found in the chemically prepared powder of the polyemeraldine salt with BF_4^-. ESR spectra were analyzed by a least square fitting for two Lorentzians with different line widths and almost the same g values. Figure 4 shows the temperature dependence of the total spin susceptibility together with that for the two ESR lines. The sharp line was confirmed to carry the Curie-like spin susceptibility and the broad line does the Pauli-like one at higher temperatures than 100 K. Below 100 K, however, the susceptibility of the broad line goes on to the Curie-like temperature dependence. The line widths are shown in Fig. 6. Here, notice that the width of the broad line shows decrease below 100 K, which is corresponding to a slope change of the spin susceptibility below 100 K in Fig. 5.



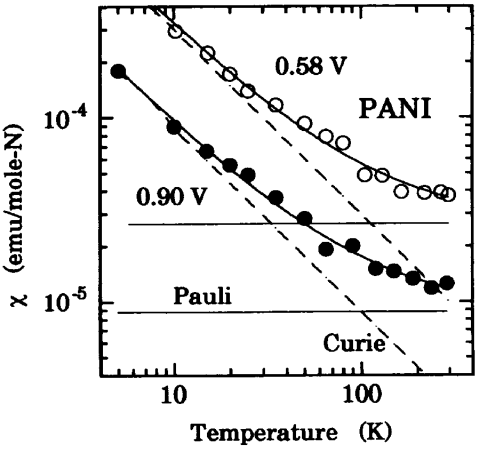


Fig. 3. (Left) Typical example of ESR spectrum analyzed by two Lorentzians for the sample at 570 mV and thickness of 7000 Å.

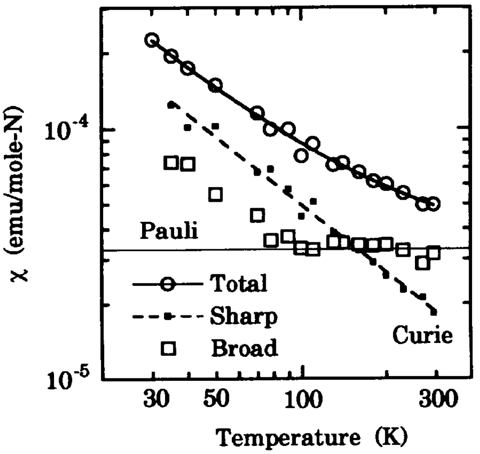
Fig. 4. (Right) The temperature dependence of the spin susceptibility dried at the potentials of 0.58 and 0.90 V and X-band. The broken and straight lines indicate Curie and Pauli contributions, respectively, estimated from the total spin susceptibility.

We should be careful with an effect of oxygen. It is well known that ESR line width in PANI is strongly enhanced up to 100 times by a presence of oxygen [5,8]. Very interestingly such broadening was observed only in the conducting state obtained by protonation with smaller pH's than 2 [5]. In the present study the ESR measurement has been done under helium and/or argon atmosphere to avoid these effect by the oxygen. Number of oxygen molecules in the sample tube for the temperature variation is estimated to be less than several ppm of a repeated unit. Then, we believe that our data never include the effect of oxygen. Further detailed study on the effect of oxygen will be reported elsewhere [9].

DISCUSSION

Now we have very interesting question to be understand; what the sharp and the broad lines are?

At first we consider the sharp line; the peak at 0.4 V in Fig. 1. It has already been reported earlier that an initial increase of the spin susceptibility was proportional to the number of injected carriers and interpreted as a polaron formation process [5]. We convinced such behavior of the initial increase around 0.3 V. And then the present data is consistent with the polaron formation. At higher potentials than the peak the spin susceptibility decreases rapidly. Usual way to explain this decrease is the bipolaron formation [5]. If a formation energy of one bipolaron is lower than that of two polarons, number of polarons indicates a peak and decrease with further increase of doping concentration [10]. The present data in Fig. 1, however, show a



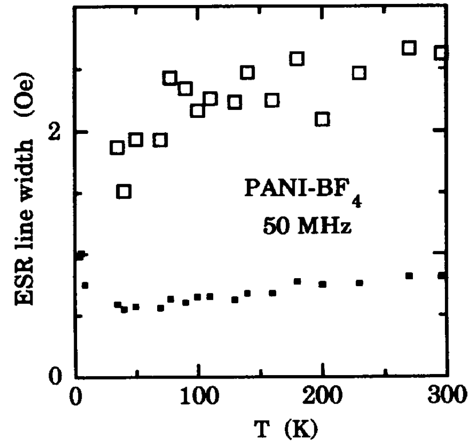


Fig. 5. (Left) The temperature dependence of the spin susceptibility for powder of the emeraldine salt with BF_4^-, measured at 29 MHz. The sharp line (▪) follows to Curie law and the broad line (□) indicates constant susceptibility at higher than 100 K.

Fig. 6. (Right) The temperature dependence of the ESR line width for the powder of emeraldine salt with BF_4^-.

formation of the second peak starting from 0.45 V accompanying with the decrease of the first polaron peak. We can say nothing on the bipolaron formation only by the susceptibility measurement. Therefore, Fig. 1 suggests the probable bipolaron formation and the polaronic lattice formation [2] or the Fermi glass formation [5,11] around the cross over potentials between two peaks.

Next, we go on to discuss the broad line; the peak at 0.6 V in Fig. 1. An important fact is that the broad line carries the Pauli-like susceptibility. As discussed above, one possible interpretation is the formation of the polaronic lattice [2]. The other is a Fermi glass state caused by strong structural disorder [5,11]. Although it is difficult to discriminate these possible origins only by the present experimental data, it may be helpful that the appearance of the second peak in Fig. 1 is rather steep. Such steep change would not presumable for the Fermi glass situation, because a degree of structural disorder should be proportional to a doping level controlled by the potential. Recent preliminary result of a spin dynamics study for the poly-emeraldine salt of pH=0 suggests that a temperature dependence of the on-chain diffusion rate $D_{//}$ below 100 K changes qualitatively from a metallic-sense at high temperatures [12]. The metallic behavior of $D_{//}$ is consistent with the Pauli-like susceptibility, interpreted by the polaron lattice. A corresponding anomaly was found in Fig. 5; a deviation of the broad line susceptibility below 100 K from the Pauli-like behavior above 100 K. Another anomalous temperature dependence has been reported at 180 K in a raman cross section which was interpreted as a critical temperature below which the polaron lattice became unstable [13]. The temperatures of the anomalies does not agree with each other, but they are possible to change depending on a doping concentration or protonation level.

In conclusion, *in-situ* ESR of PANI gave two signals with different characters; 1) formation of the Curie susceptibility (polaron) and 2) formation of the Pauli-like susceptibility above 100 K. The latter was interpreted to concern with a formation of the polaron lattice. The anomaly was suggested around 100 K.

ACKNOWLEDGEMENTS

One of authors (K.M.) is grateful to Dr. V. M. Geskin for useful discussions. This work is supported partly by Grant in Aid for Scientific Research of The Ministry of Education in Japan.

REFERENCES

1 See, for example, the proceedings of ICSM'90, SantaFe, 1990.

2 a) J. M. Ginder, A. F. Richter, A. G. MacDiarmid and A. J. Epstein, Sol. St. Commun., 63 (1987) 97, b) S. Stafström, J. L. Brédas, a. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang and A. G. MacDiarmid, Phys. Rev. Lett., 59 (1987) 1464.

3 a) K. Mizoguchi, M. Nechtschein, J. P. Travers and C. Menardo, Synth. Met., 29 (1989) E417, b) K. Mizoguchi, M. Nechtschein, J. P. Travers and C. Menardo, Phys. Rev. Lett., 63 (1989) 66 and c) K. Mizoguchi, M. Nechtschein and J.-P. Travers, Synth. Met., 41-43 (1991) 113.

4 M. E. Jozefowicz, R. Laversanne, H. H. S. Javadi, A. J. Epstein, J. P. Pouget, X. Tang and A. G. MacDiarmid, Phys. Rev. B, 39 (1989) 12958.

5 M. Nechtschein, F. Genoud, C. Menardo, K. Mizoguchi, J. P. Travers and B. Villeret, Synth. Met., 29 (1989) E211.

6 H. Kuzumany, N. S. Sariciftci, H. Neugebauer and A. Neckel, Phys. Rev. Lett., 60 (1988) 212.

7 M. Lapkowski, Synth. Met., 35 (1990) 169.

8 H. H. S. Javadi, R. Laversanne, A. J. Epstein, r. K. Kohli, E. M. Scherr and A. G. MacDiarmid, Synth. Met., 29 (1989) E439; This paper reported also two kinds of signals, Lorentzian and Gaussian instead of two Lorentzian in the present paper. Other details also differ from each other, for example, the broad line carries Curie-susceptibility instead of Pauli-like susceptibility in the present.

9 K. Mizoguchi, T. Obana, S. Ueno and K. Kume, in preparation.

10 M. Nechtschein, F. Devreux, F. Genoud, E. Vieil, J. M. Pernaut and E. Genies, Synth. Metl. 15 (1986) 59.

11 F. Wudl, R. O. Angus, F. L. Lu, P. M. Allemand, D. J. Vachon, M. Nowak, Z. X. Liu and A. J. Heeger, J. Am. Chem. Soc., 109 (1987) 3677.

12 K. Mizoguchi, J.-P. Travers and M. Nechtschein, in preparation.

13 M. Bartonek and H. Kuzumany, Synth. Met., 41-43 (1991) 607.