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EPR STUDIES OF THE CHARGING PROCESS OF POLYANILINE ELECTRODES

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EPR measurements have been done with a polyaniline coated platinum electrode at various stages of oxidation. The measurements were carried out *in situ* conditions in both aqueous and non-aqueous solutions. At the initial stage of anodic oxidation, electron spins accumulate in the polymer film upto 1×10^{20} spins/gram and then decrease gradually with increasing charge of electrolysis.

Studies of conducting polymers are attracting interests of various fields of researches. Studies by the electron paramagnetic resonance are particularly of interest since EPR measurements provide valuable information about the polymer structure as well as the electric conduction mechanism.

As for polypyrrole, EPR studies on this material seem to have been initiated by Dascola et al., as early as 1966.1,2) Using both chemically and electrochemically prepared polymers, they studied EPR signals as a function of temperature in correlation with the electric conductivity. High conductivity of polypyrrole was already mentioned by them. Recently, Scott et al.3) have discussed the spin density of polypyrrole from the viewpoint of electric conduction mechanism. According to them, the EPR signal intensity of neutral (reduced) polypyrrole at room temperature is strongly affected by the amount of oxygen absorbed by the polymer. The intensity goes up as the oxygen uptake increases and reaches maximum at about 0.3% of oxygen. After passing the maximum, the intensity goes down monotonically to the original value at about 0.6% of oxygen uptake. On the other hand, the change in film conductivity is more drastic and increases by an amount of at least four orders of magnitude for the first 0.2% of oxygen uptake and then becomes invariant for further oxygen uptake. Pumping at any stage above 0.5% weight uptake removes only a small amount of oxygen (0.2%) and does not affect the conductivity. Based upon these observations, Scott et al. concluded that the source of EPR signal has no direct correlation with the species responsible for the electric conduction. More recently, Genies and Pernaut4) have described that the number of spins in polypyrrole has a maximum at a certain electrode potential followed by the decrease at higher potentials.

We have found that a similar conclusion can be applied to polyaniline when it is *in situ* oxidized in electrolytic systems. In the following part of this brief communication, we will show the results of observations in both aqueous (0.1 M H_2SO_4) and non-aqueous (1.0 M lithium perchlorate in propylene carbonate) solutions.

The absorption line of polyaniline was found to be Lorentzian in shape having g-value of 2.0024 ± 0.00008 at room temperature. The absorption was observed even with a specimen of "completely" reduced but the line width of it varied from 1.4 to 2.5 G by some unknown reasons. On the other hand, the line width became constant (0.9 G) upon slight oxidation of the film and was almost unchanged for further oxidation. No significant change in line shape was observed by the nature of solution, aqueous or non-aqueous.

A platinum wire (0.2 mmϕ, 10 mm in effective length) was sealed at the bottom of a thin glass capillary (1.8 mm in outer diameter, 70 mm long) which was attached to a larger glass tube (6 mm in inner diameter) at the upper end. The platinum was coated with polyaniline prepared by constant potential anodization (0.8 V SCE, 100 mC) in 1.0 M sulfuric acid solution. Both the counter and reference electrodes were placed in the upper glass tube and the cell assembly was set in such a position as to locate the polymer electrode at the center of the EPR cavity. The polymer electrode was first cathodized at a sufficient negative potential for a long time until the cathodic current virtually diminished. The potential was then elevated step by step with an interval of 0.025 V. At each potential, time course of anodic current and that of the total charge passed were recorded until the current became virtually null, and then the polarization circuit was disconnected to measure both the EPR signal and the electrode potential at open circuit.

Result obtained in non-aqueous solution is shown in Fig. 1. Although the figure indicates the change in signal intensity during the anodic going polarization, a similar curve with a small hysteresis was also observed when the polarization was reversed towards the cathodic direction. An entirely similar curve behavior was observed when the measurement was carried out in aqueous solution : maximum spin density appeared at 0.15 V (vs.SCE).

Figures 2 and 3 show the correlation between log[spin density] and the electrode potential for aqueous and non-aqueous solutions, respectively. The slopes of the linear part are 40[5] and 61 mV/decade for Figs. 2 and 3, respectively. This indicates that the potential of polyaniline electrode is governed by the Nernst's equation;

$E = E^\circ + (RT/nF)\ln[\text{paramagnetic electrons}]$

where apparent n is equal to unity for non-aqueous system, while it is 1.5 for aqueous system. It should be noted that the potential region where the Nernstian behavior is observed exactly coincides with the potential region where anodic current starts to grow in the cyclic voltammograms. The values of Nernstian slope, 40 and 60 mV, are, however not the subject of the simple consideration since

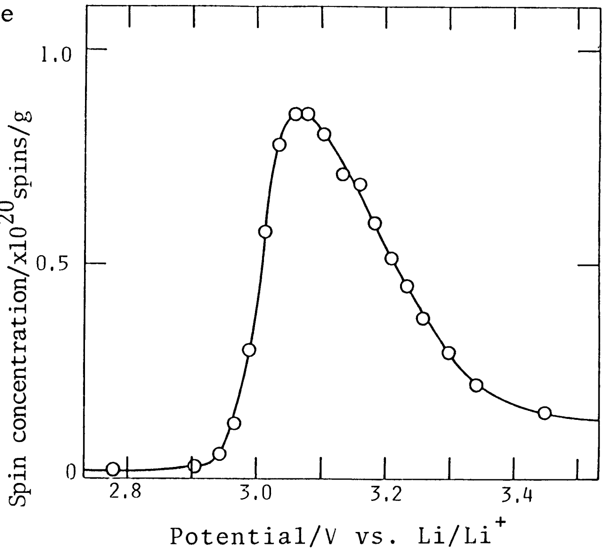

Fig.1. Change in spin concentration of polyaniline electrode during the anodic polarization in a propylene carborate solution.

the coulombic efficiency for generating electron spins was found ca. 50% in non-aqueous system while it was almost 100% in aqueous solution.

In this connection, the work of Feldberg[6)] may be informative, who pointed out that the Faradaic current appearing in conducting polymer electrode system cannot be discriminated in principle from the non-Faradaic charging current and, if the polymer electrode is of fibril structure, the contribution of the charging current will become exceptionally large. Although Murray's group[7)] seems somewhat skeptic for the fibril structure of polypyrrole film, this problem has been left for further study. We have to be more careful of discussing the coulombic efficiency.

At the present stage of our experiments, we have to restrict our conclusion as follows.

1. Upon anodic oxidation, polyaniline electrode accumulates electron spins monotonically with increasing charge in the film.
2. The coulombic efficiency for generating electron spins seems to be affected by the nature of electrolyte solution.
3. At the stage where electron spins are being accumulated in the film the electrode potential is governed by the Nernst's equation at least qualitatively.
4. The facts described above are applicable only to the initial stage of oxidation and in the succeeding stage of oxidation electron spins tend to decrease gradually.

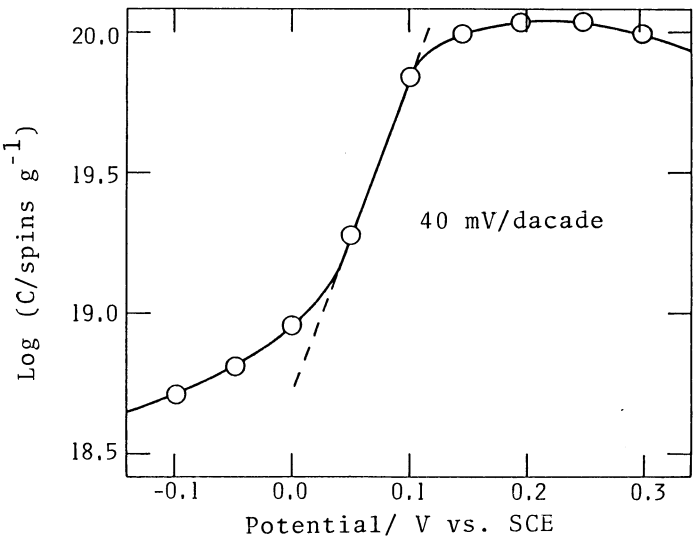

Fig.2. Correlation of log (spin concentration) against electrode potential. Solution : 0.1 M H_2SO_4.

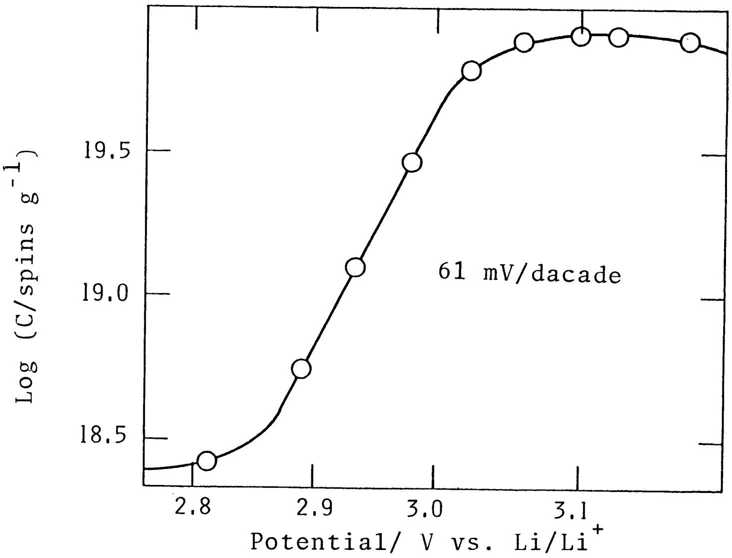

Fig.3. Correlation between log (spin concentration) and electrode potential. Solution : 1.0 M $LiClO_4$ in propylene carbonate.

According to the recent work of Wrighton and his colleagues,[8)] polyaniline electrode immersed in 0.5 M $NaHSO_4$ solution is less conductive at both negative and positive sides of 0.4 V(SCE) and the change in resistivity at both sides of the potential amounts to six orders of magnitude. The last point of our conclusions together with the resistivity change found by Wrighton et al. indicate that the electron spins created in the film have no direct correlation with the electric conductivity of the polyaniline film.

From the similar results obtained with dry samples of polypyrrole, Scott and his colleagues have proposed the bipolaron theory for the conduction mechanism.(3) This may be applied to our case, too.

Fuller examinations on the EPR behavior of polyaniline electrodes are now in progress.

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Referinces

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5) This value was determined by connecting only two points in Fig. 2. Accordingly. if we made a more precise measurement, the potential region where the linearity holds might become slightly narrower than indicated. If this were the case, the slope would become slightly smaller than 40 mV and would never reach 60 mV. The point to bo stressed here is that the discussion of the observed slope should be careful.

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