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## Mechanism of Electropolymerization of Pyrrole in Acidic Aqueous Solutions

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Mechanism of electrochemical polymerization of pyrrole (Py) on a Pt electrode in acidic aqueous solutions was studied by means of potentiostatic measurements, cyclic voltammetry and chronopotentiometry. Pyrrole molecule appeared to be initially oxidized via two-electron transfer step to produce oxidized pyrrole ion (Py<sup>+</sup>), which was coupled with a non-oxidized pyrrole to yield a dimerized species, Py-Py. The Py-Py thus formed was further oxidized again via two-electron transfer step, which was followed by coupling with non-oxidized monomer and by concomitant expulsion of a H<sup>+</sup>. Then the latter chain extension process was repeated. The chain extension and polypyrrole oxidation reactions occurred competitively.

### Introduction

Recently interest in polypyrrole as a conducting polymer has been increasing rapidly.<sup>1-4</sup> Polypyrrole has received considerable interest because it can increase the stability of photoelectrodes used in converting solar energy to electrical or chemical energy.<sup>5</sup> However, there are only a few reports concerning with the detailed study on the mechanism of pyrrole polymerization under oxidizing conditions.<sup>6-9</sup>

Lundström and coworkers<sup>6</sup> suggested that the electropolymerization of pyrrole in the presence of fluoroborate (BF<sub>4</sub><sup>-</sup>) ion was initiated by the oxidation of BF<sub>4</sub><sup>-</sup>. Since the oxidation of BF<sub>4</sub><sup>-</sup> does not occur until +3.0V, their suggestion is impossible to admit. Moreover, the electropolymerization of pyrrole on a Pt electrode could be achieved without BF<sub>4</sub><sup>-</sup> in this study.

The literatures assume that the polymerization reaction is initiated by removal of one electron from pyrrole.<sup>7-9</sup> But the experimental data are insufficient to support this assumption. Diaz<sup>7</sup> proposes that the next step should involve the coupling of two radical cations on the ground that the concentration of the neutral aromatic species is zero at the electrode and negligible in the double layer region. Polymerization in solution was suggested similarly between cation radicals.<sup>8</sup> Considering the dimerization of small cation radicals being an unusual step, Pletcher *et al.* suggest that the dimer

should form between cation radical and neutral pyrrole with the expulsion of H<sup>+</sup> and two electrons.<sup>9</sup> Thus the mechanism of pyrrole electropolymerization is still not well understood.

Hence it is attempted to investigate the pyrrole polymerization process on a Pt electrode in acidic aqueous media for better understanding of the polymerization. To elucidate the electropolymerization in this study Tafel plots, cyclic voltammograms and chronopotentiograms were utilized.

### Experimental

All chemicals, if not otherwise mentioned, were reagent grade and used without further purification. Pyrrole (Fluka AG, Purum) was vacuum distilled before use. All solutions were deoxygenated with a stream of nitrogen gas within an electrochemical cell before measurement. pH of solution was adjusted with either H<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>PO<sub>4</sub><sup>-</sup> or H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> buffer solutions.

The electrochemical experiments were carried out in a three electrode system with a working electrode and a Pt gauze electrode separated by a Vycor frit and a S.C.E. reference electrode connected to the analyzing compartment through a Vycor frit. All the potentials given here are referred to S.C.E.. For most experiments, the working electrode was a Pt wire (area 0.19 cm<sup>2</sup>) sealed into glass, which was freshly conditioned prior to each experiment.

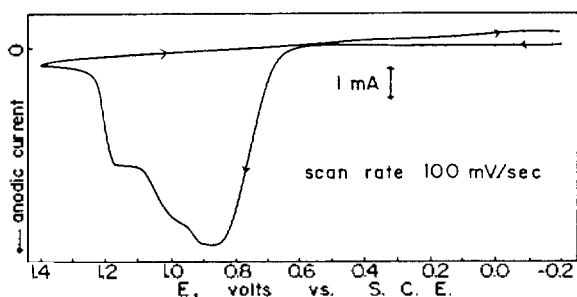


Figure 1. Cyclic voltammogram of 0.10 M pyrrole in 1.0 M  $\text{HNO}_3$  at a Pt electrode.

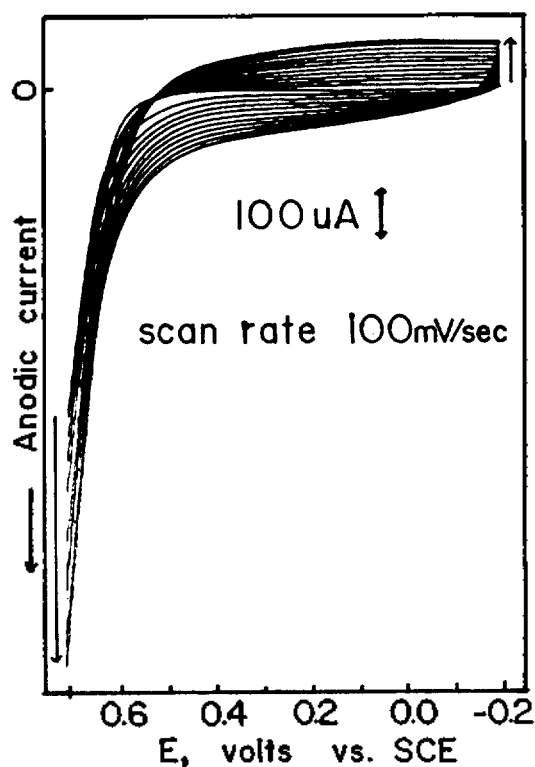


Figure 2. Repeated cyclic voltammograms of 0.10 M pyrrole in 1.0 M  $\text{HNO}_3$  at a Pt electrode. Total scan number was 11.

A Princeton Applied Research Model 273 potentiostat/galvanostat and RE0091 X-Y recorder were used for electrochemical experiments. An Apple II microcomputer with a laboratory-built interface card was utilized for the transient data acquisition.

### Results and Discussion

Figure 1 shows the first cyclic voltammogram of 0.10 M pyrrole in 1.0 M  $\text{HNO}_3$  with a Pt electrode at a scan rate of 100 mV/sec. The anodic current leading to a broad peak at about 0.90V begins to flow near 0.55V and beyond the maximum several overlapping oxidation peaks are discernible. When the direction of scan was reversed before the maximum but larger than 0.55V, the current increased progressively with the number of cycles. Oxidation current around 0.2V appeared from the second sweep and continuously grew with cyclings as shown in Figure 2. The currents near 0.20V and 0.00V are attributed to oxidation and reduction of

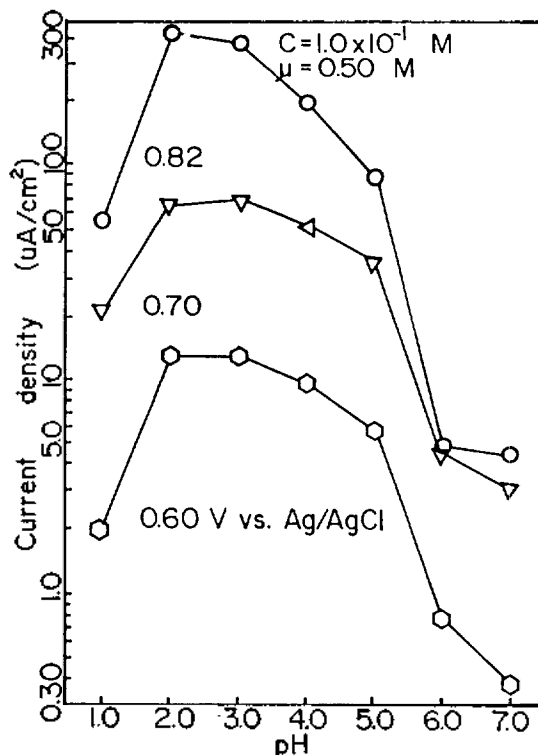


Figure 3. Steady-state anodic currents at given potentials vs. pH. Ionic strength was kept at 0.50 M.

polypyrrole, respectively, which was confirmed by observing no further increase in current of a polypyrrole coated Pt in pyrrole free solutions. Thus, initiation and extension of pyrrole polymerization should occur at potentials larger than 0.55V under the experimental condition, which is in good agreement with a previous report.<sup>10</sup>

Steady-state currents at given potentials vs. pH are presented in Figure 3. The ionic strength was kept at 0.50 M. Optimum pH region for the electropolymerization is seen between 2.0 and 3.0. In basic solutions, polypyrrole was difficult to obtain probably because  $\text{OH}^-$  reacts with an intermediate to result in termination of the polymerization. Since  $\text{p}K_a$  of pyrrole is 11.2, the major species in the bulk of acidic pyrrole solution (pH 3.0) is protonated pyrrole. However, within electrical double layer where electron transfer reactions may take place, neutral pyrrole molecules are probably dominating over protonated pyrrole based on the following experimental evidences. The potential of zero charge of a Pt electrode is about 0.19V, so neutral pyrrole is less repelled than protonated pyrrole from the electrode at anodic potentials larger than 0.19V. Pan and Stair have reported that neutral pyrrole is readily chemisorbed via electron donation from a  $\pi$ -bonding orbital to a metal surface.<sup>11</sup> In addition, according to Funt and Lowen the initiation currents are independent of pyrrole monomer concentration,<sup>12</sup> indicating that adsorption on an electrode precedes the oxidation which leads the polymerization. Thus adsorbed neutral pyrrole probably initiates the polymerization.

Figure 4 shows quasi-steady state polarization curves (Tafel Plots) of pyrrole over a wide range of concentration in 1.0 M  $\text{HNO}_3$  at a Pt electrode. Tafel plot was obtained from a reproducible, single linear sweep voltammogram from -0.2V to an appropriate oxidation potential with a freshly prepared

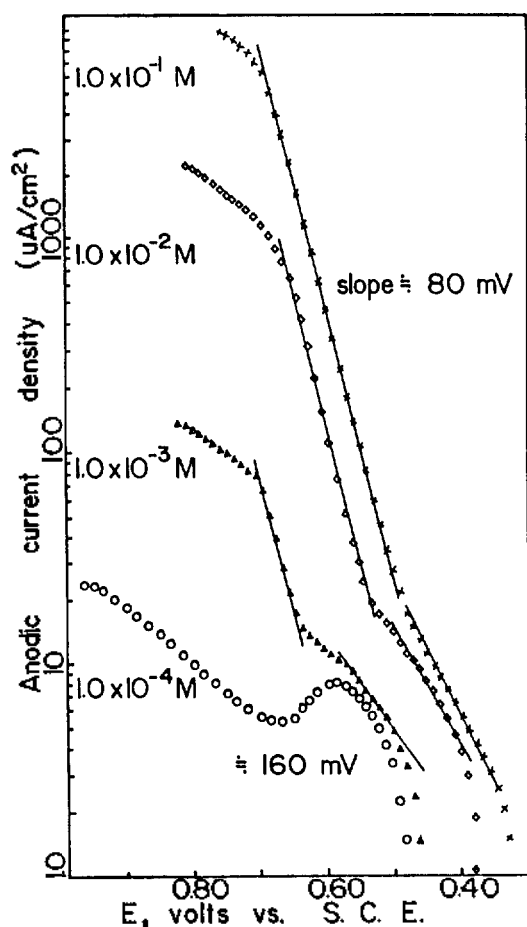


Figure 4. Anodic quasi-steady state polarization curves for a wide range of pyrrole concentrations in 1.0 M HNO<sub>3</sub> at a Pt electrode.

Pt electrode. Scan rate was 0.5mV/sec, however, even lower scan rates produced essentially identical plots. It is noted that down to  $1.0 \times 10^{-3}$ M pyrrole the plots exhibit two Tafel slopes of approximately 160mV and 80mV over low and moderate polarization regions, respectively, followed by a sharp deviation over high-polarization region. Crossing of the two Tafel slopes at a point in such a way as in Figure 4 suggests that two parallel reactions are occurring. Apparently polypyrrole film may be formed below 0.55V at such slow scans when the pyrrole concentration is higher than 0.01M. Tafel slope over low polarization region probably corresponds to the polypyrrole oxidation. Current density at or below  $1.0 \times 10^{-4}$ M pyrrole was very low and largely obscured by the current due to platinum oxides around 0.60V. Polymerization from less than  $10^{-4}$ M pyrrole is, therefore, considered minimal under the conditions of steady state.

Tafel plots derived from the linear sweep voltammograms under the condition of stirring the solution are compared with those obtained without stirring in Figure 5. It is particularly noticed to observe the decrease of Tafel slope for  $1.0 \times 10^{-6}$ M pyrrole to about 85mV by convection. This decrease is associated with the reduction of concentration polarization. Moreover, as the pyrrole concentration increases to 0.10 M, the Tafel slope is further decreased to about 80mV. Thus, if the concentration polarization is effectively removed, the Tafel slope arising mainly from charge transfer in  $1.0 \times 10^{-6}$ M pyrrole at a Pt electrode should be less than 85mV. Now, at an anodic potential, E, the current is gene-

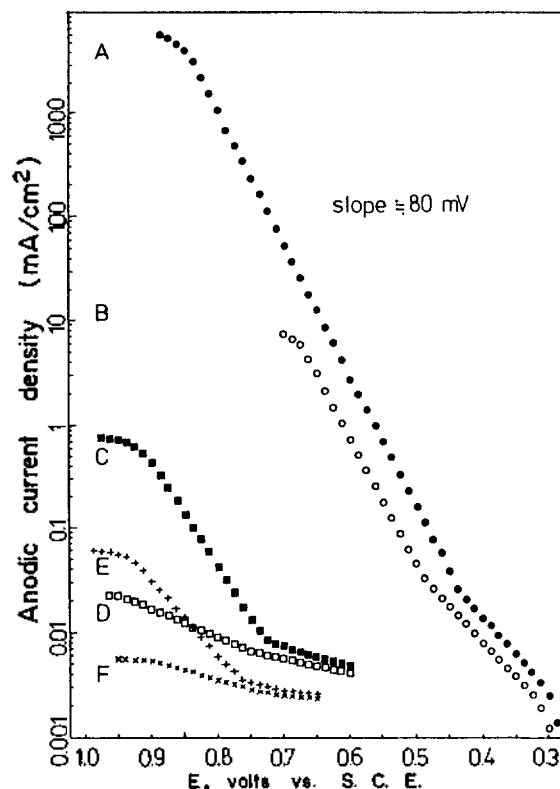
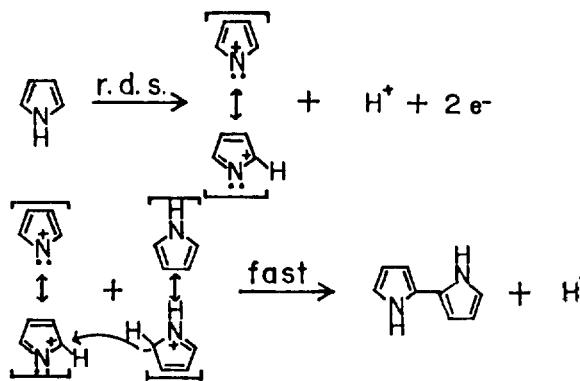


Figure 5. Comparison of polarization curves (A,C,E) of stirred solutions with those (B,D,F) of respective unstirred ones. Concentrations of pyrrole (M): A and B, 0.10; C and D,  $1.0 \times 10^{-4}$ ; E and F,  $1.0 \times 10^{-6}$ .



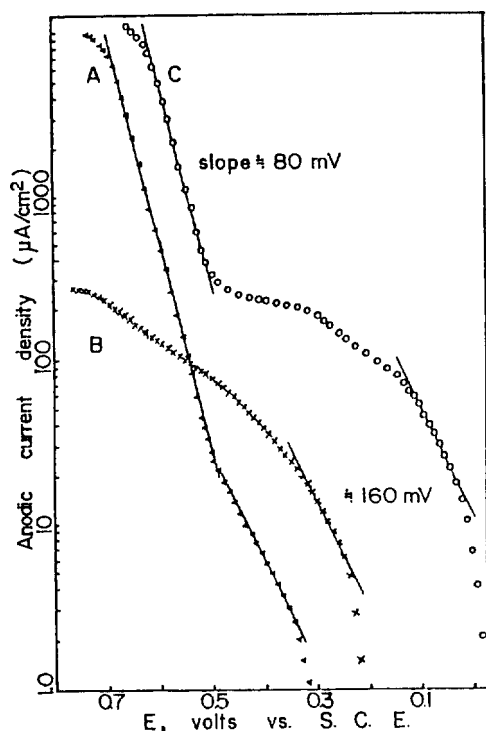
Scheme 1

rally given by

$$i = i_0 \exp \{nF(1-\alpha)E/RT\} \quad (1)$$

where  $i_0$ ,  $\alpha$ , and  $n$  are exchange current, transfer coefficient, and number of electrons transferred at the rate determining step, respectively. If  $\alpha$  is assumed to be about 1/2 as usual, the observed Tafel slope of less than 85mV suggests that the electron transfer reaction from pyrrole molecule to the electrode is apparently dominant over the oxidation reaction of polypyrrole and then  $n$  in Eq(1) should be estimated to be equal to two at room temperature.

Based on these experimental results, the pyrrole polymerization appears to be initiated by removal of two electrons from an adsorbed neutral pyrrole molecule to produce a reactive intermediate,  $\text{Py}^{\bullet+}$ , followed by a rapid dimerization with a neutral pyrrole as proposed in Scheme 1. The former



**Figure 6.** Anodic quasi-steady state polarization curves for A: a Pt electrode in 0.10 M pyrrole/1.0 M HNO<sub>3</sub>; B: a polypyrrole coated Pt in 1.0 M HNO<sub>3</sub>; and C: a polypyrrole coated Pt in 0.10 M pyrrole/1.0 M HNO<sub>3</sub>.

step is considered as the rate determining step. The two-electron process may be supported by the observation that electrolysis of N-methylpyrrole occurs via an intermediate dicarbocation.<sup>13</sup> In the present system, however, Py<sup>+</sup> is considered to be more stable than dicarbocation. The proposal in Scheme 1 is somewhat similar to that suggested recently by Pletcher *et al.*,<sup>9</sup> that is, the pyrrole radical cation formed by removal of one electron reacts with a neutral pyrrole to form a dimer cation followed by removal of another electron and H<sup>+</sup> to result in a neutral dimer. It is not possible to distinguish whether the initiation reaction proceeds via two fast one-electron steps having similar oxidation potentials or via a two-electron step. In fact, an aromatic radical species are generally not stable in aqueous acidic solutions and therefore it is probable that a cationic radical is further oxidized to a cation. However, the proposal<sup>6</sup> that oxidation of BF<sub>4</sub><sup>-</sup> ions is a necessary step in the polymerization is not acceptable since polypyrrole film can be formed in the absence of BF<sub>4</sub><sup>-</sup> ions.<sup>6</sup> Another literature by Diaz<sup>7</sup> suggested that the dimerization occurred between two pyrrole cation radicals which are formed initially by removal of an electron from each pyrrole molecule. However, the dimerization of cation radical of small concentration does not seem to be very probable. The polymerization is observed even when the potential is as low as 0.5V shown in Figure 5 if the scan rate is extremely slow. Furthermore, Tafel slope should be expected to be 120mV if the mechanism by Diaz<sup>7</sup> were correct.

To understand the accompanying chain extension step, Tafel plots are obtained under three different conditions and shown in Figure 6: A is a plot of a Pt electrode in 0.10M pyrrole/1.0M HNO<sub>3</sub>; B is that of a polypyrrole coated Pt in 1.0M HNO<sub>3</sub>, and C is that of a polypyrrole coated Pt in 0.10M pyrrole/1.0M HNO<sub>3</sub>. Curves A and B have the same

slopes of about 80mV over high polarization region where the polymer is extended on the surface of polypyrrole coated Pt electrode. In C, no such reaction is possible. Furthermore, since convection enhanced the currents of 0.1M pyrrole solution at high potentials as shown in Figure 5, electroactive species is not the polypyrrole on the electrode, but pyrrole supplied from the bulk. Tafel slope of 80mV indicates that the number of electrons participated in the rate determining step of the chain extension should be again two. Therefore, the chain is extended with the oxidation of neutral pyrrole by a two-electron removal process just like in Scheme 1, followed by coupling the intermediate, Py<sup>+</sup>, to the end of the polymer chain at Pt. In this case,  $\alpha$  is computed to be 0.62, which is a reasonable value.

The polypyrrole oxidation and the chain extension reactions occur competitively, as illustrated in Figure 4 and 5. Furthermore, polypyrrole film has a conducting character, only if the film is in the oxidized form. Hence, the oxidation of polypyrrole is a prerequisite for the growth of polypyrrole film. Overall polymerization process has been found to involve about 2.2 electron transfer per pyrrole at moderate potentials.<sup>9</sup> The number of electrons participated in the overall reaction was verified to agree well within experimental uncertainty with a result obtained by chronopotentiometry in our laboratory, 2.2<sup>±</sup>0.1. Since two electrons are transferred per pyrrole unit in the polypyrrole, the additional fraction of electrons transferred should originate from the oxidation of polypyrrole. The authors tend to support the generally accepted scheme<sup>9</sup> that the oxidation of polypyrrole film requires one electron transfer per four pyrrole units in polypyrrole.

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