

# Electrochemical Polymerization of Pyrrole in Aqueous Solutions

## 1. Comparison of Solution-Surface-Growth and In-Solution-Growth Methods

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In search of conducting polymer films that have better mechanical and electrical properties, numerous investigators<sup>1,2</sup> have electropolymerized pyrrole in a variety of organic solvents. There have been relatively fewer reports on polymerization in aqueous solutions<sup>3,4</sup>. Warren *et al.*<sup>5</sup> recently reported formation of free-standing polypyrrole films by anodic deposition from aqueous electrolytes containing a large variety of anions. We found that conducting polypyrrole (PPy) could be readily synthesized electrochemically along the surface of aqueous solution when proper anions were present in the solution.

In this communication we present electrochemical synthesis of conducting PPy in aqueous solution containing large amphiphilic anions (in-solution-growth) and synthesis at solution/gas interface (solution-surface-growth).

Pyrrole(Fluka) was used after vacuum distillation over calcium hydride ( $\text{CaH}_2$ ) to eliminate the oxidized impurities<sup>6</sup>. The clear pyrrole was stored in dark room at 4°C under nitrogen atmosphere. Sodium dodecyl sulfate(SDS), *p*-toluene sulfonic acid (*p*-TSA), and tetraethyl ammonium *p*-toluene sulfonate { $\text{Et}_4\text{N}(p\text{-TS})$ } (Aldrich) were used as supporting electrolytes without further purification. All electrolyte solutions were prepared from doubly distilled water whose conductivity was less than  $10^{-7} \Omega^{-1}\text{cm}^{-1}$ . A platinum wire(geometric surface area = 0.24  $\text{cm}^2$ ) and a platinum plate(geometric surface area = 3.4 $\text{cm}^2$ ) were used as the working electrode for the solution-surface-growth and the in-solution-growth method, respectively. For the surface-growth studies, the electrochemical polymerization was carried out with the platinum wire that was brought into contact with the surface of the solution as shown in Figure 1. For the in-solution-growing electrolysis, the platinum plate, that had been polished to a final smoothness with slurry of alumina polishing powder of about 0.1 micron, was used immersed in the electrolyte solution. The reference electrode was a saturated calomel electrode and the potential data given here are referred to this electrode. The solutions were deaerated with stream of nitrogen gas which had been purified by passing through a tube of hot copper shred, and all measurements were performed under the nitrogen atmosphere.

Figure 2. shows a typical cyclic voltammogram (CV) for the growth of polypyrrole (PPy) film on a platinum electrode in aqueous 0.10M SDS-solution. It appears that the anodic current rising from about 0.50V vs SCE in the first scan, is associated with the oxidation of pyrrole. From the second scan, the anodic current appeared at less positive potentials and increased gradually. According to this cyclic voltam-

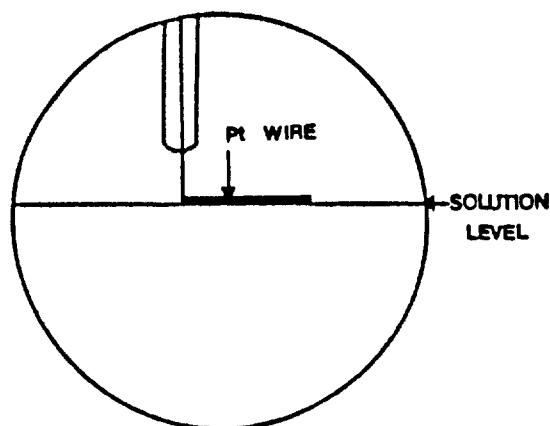


Figure 1. Schematic diagram of working electrode for solution-surface-growth electrolysis.

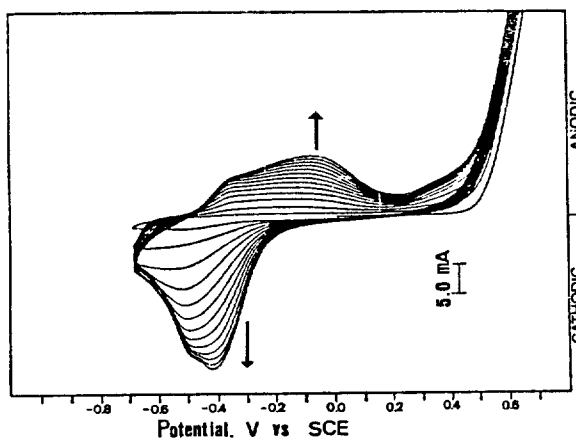
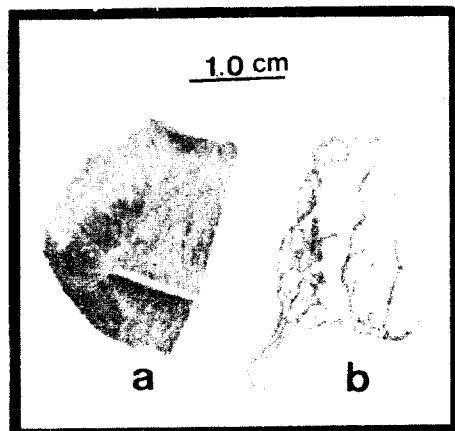


Figure 2. Typical cyclic voltammogram for the formation of polypyrrole in 0.20 M pyrrole/0.10 M sodium dodecyl sulfate solution.

mogram and the previous results by one of the authors<sup>7</sup>, the electropolymerization of pyrrole can be sustained near potential of 0.7V in the solutions tested here. Therefore, the potentiostatic polymerization of pyrrole was performed at 0.7V in aqueous solutions of 0.20M pyrrole/0.10M electrolytes. Mass of polypyrrole could be grown along the solution surface using the appropriate electrolytes containing amphiphilic anions. This was possible due to reduction of surface tension of the solutions. Typically, the PPy formed on the surface of solution were in the shape of a plate or fibrils



**Figure 3.** Photographs of the Conducting Polypyrrole Synthesized by the Solution-Surface-Growth Method. (a) PPy-film grown on 0.10 M *p*-TSA Solution. (b) PPy-fiber grown on 0.10 M SDS Solution.

**Table 1. Rating of Electrolytes as Solution-Surface-Growth (S.S.G.) and In-Solution-Growth (I.S.G.) Promoter**

Electrolyte	S.S.G.		I.S.G.	
	Film Quality	Growth rate	Film quality	Growth rate
<i>p</i> -TSA	Smooth film <sup>a</sup>	Rapid	Smooth film <sup>a</sup>	Rapid
Et <sub>4</sub> N( <i>p</i> -TS)	Smooth film	Moderate	Smooth film	Moderate
SDS	Fibrous <sup>b</sup>	Rapid	Smooth film <sup>b</sup>	Rapid
Et <sub>4</sub> NBF <sub>4</sub>	None	No Growth	Rough film	Slow
KCl	None	No Growth	Powdery	Slow

<sup>a</sup> more flexible than others, <sup>b</sup> more brittle than the others.

as shown in Figure 3 depending on the electrolyte. A relative rating of electrolytes as promoters for the electropolymerization was summarized in Table 1.

Conductivity and elemental analysis data of the PPy-films prepared from aqueous *p*-TSA solution are listed in Table 2. The PPy-film obtained by the solution-surface-growth method resulted in better conductivity than that grown by the in-solution-growth method. However, the data of elemental analyses of the two samples were in agreement with each other within the experimental error. The ratio of pyrrole unit to anion, [Py]/[A], in the PPy-films was calculated to be 2.2 to 2.3 from the elemental analysis data. This indicates that units of the conducting PPy-films are [(Py-Py)<sup>+</sup>A<sup>-</sup>]<sub>x</sub>, in contradiction to the generally accepted composition for the film including an inorganic anion, [(Py-Py-Py-Py)<sup>+</sup>A<sup>-</sup>]<sub>x</sub>.<sup>9</sup> The

**Table 2. Conductivity and Elemental Analyses Data of PPy-films Prepared in 0.10 M *p*-TSA Solution.**

Growing Method	Conductivity <sup>a</sup> (Ω <sup>-1</sup> cm <sup>-1</sup> )	Elemental Analysis(%)			Py/A
		C	H	N	
In-Solution	120	58.8	4.6	9.7	2.2
Solution-Surface	200	59.3	4.4	9.7	2.3

<sup>a</sup> Measured by 4-probe conductance meter<sup>8</sup>.

cyclic voltammograms for the PPy-films prepared in the aqueous solution of 0.10M *p*-toluene sulfonic acid (In-Solution-Growth Method) and on the surface of solution (Solution-Surface-Growth Method) exhibited same pattern of redox behaviour under the potential range used herein.

Based on the above facts, we conclude that the PPy-film obtained by the solution-surface-growth method has chemical and electrochemical properties similar to that obtained by the in-solution-growth. However, the solution-surface-growth technique gives improved mechanical and conducting properties of the PPy-films.

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