

EFFECT OF ULTRASONIC WAVE ON THE ELECTROPOLYMERIZATION OF PYRROLE *

YANG Jing (杨静) and LI Yongfang (李永舫)**

(Laboratory of Organic Solids, Institute of Chemistry, Academia Sinica, Beijing 100080)

ABSTRACT

Electropolymerization of pyrrole under ultrasonic field at 20kHz was performed in a series of aqueous and propylene carbonate (PC) solutions. The ultrasonic wave with moderate intensity at the power of 44W, which is the power threshold of the ultrasonic generator used in this work to produce cavitation effect, enhance the conductivity and tensile strength of the polypyrrole films as prepared. However, too high intensity of the ultrasonic wave is harmful to the polymerization.

INTRODUCTION

Electrochemical polymerization of pyrrole has been widely employed to obtain flexible and conductive polypyrrole (PPy) films. It has been noticed that the conductivity and mechanical properties of PPy films are much dependent on their polymerization conditions, such as the nature of anions^[1-3], pH values^[4], solvents of the electrolyte solutions^[5], the nature of the working electrode^[6,7], and temperature^[8] etc. Therefore, searching for the most favourable conditions in the electropolymerization to prepare the PPy films with higher conductivity and better tensile strength is still the main subject in the study of conducting polypyrrole.

Ultrasonic wave was ever used in the electropolymerization of thiophene^[9]. Flexible polythiophene films with higher conductivity of 130—150 S cm⁻¹ and the tensile strength of 90MPa were obtained, fairly better than that without the irradiation of ultrasonic wave. Considering the similar mechanism of the electropolymerization of thiophene and pyrrole, the effect of ultrasonic wave on the electropolymerization of pyrrole was studied in this paper.

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** To whom correspondence should be addressed.

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EXPERIMENTAL

Electropolymerization of pyrrole was performed galvanostatically at 2mA cm^{-2} in the solution of 0.1mol/L pyrrole, 0.2mol/L supporting electrolyte with or without the irradiation of ultrasonic wave. Two stainless steel plates were used as working and counter electrodes. The acidity of the aqueous solutions was adjusted to $\text{pH}=3$ by adding corresponding acid solutions. The polymerization was performed in a glass cell with a diameter of 2cm . The cell was put in the ultrasonic water bath with the size of $30\text{cm}\times 45\text{cm}$ when applying the ultrasonic wave. The ultrasonic wave was produced by a CSF-250-3 Ultrasonic Generator whose power was set to 44W , 55W , 66W and 77W respectively to change the intensity of the ultrasonic wave. The intensity of the ultrasonic wave of 44W , mentioned in the following of this paper, means that it is produced by the generator at the power of 44W . The other intensity is also referred to the generator power.

Potentiostatic polymerization of pyrrole and cyclic voltammetry were performed in a three electrodes cell with a Pt disc of 0.07cm^2 at area as working electrode, a Pt plate as counter electrode and a saturated calomel electrode (SCE) as reference. Potential scan rate is 20mV/s in the cyclic voltammetry. Traditional four probe method was used in the conductivity measurement. Mechanical properties of the polypyrrole films were measured at room temperature with a stretching rate of 1mm/min by an Instron 1122 Universal Testing Instrument. The thickness of the films for the measurements of conductivity and mechanical properties is ca. $20\text{--}40\mu\text{m}$.

RESULTS AND DISCUSSION

Effect of ultrasonic wave on the reaction rate of polymerization

The potentiostatic polymerization of pyrrole in 0.1mol/ml pyrrole, 0.2mol/ml TsONa aqueous solution at $\text{pH } 3$ was performed under the ultrasonic field with different intensity. The chronoamperograms are shown in Fig.1. At the potential of 0.7V vs. SCE, the polymerization current under ultrasonic field is stronger than that without the irradiation of the ultrasonic wave. The current jumps to a value after the potential is on. Then it goes in various ways for different conditions. The current decreases with time till ca. 15 seconds for the case without ultrasonic irradiation, which is due to the diffusion of pyrrole and the electrolyte anions, while it increases with time gradually for the case under the ultrasonic field. The phenomenon may be resulted from the elimination of diffusion by the micro-agitation effect of the

ultrasonic field. Fig.1 also shows that the stronger the intensity of the ultrasonic field is, the larger is the polymerization current. The behavior at 0.75V vs. SCE is similar to that at 0.7V vs. SCE. So, it can be concluded that the ultrasonic wave accelerates the electropolymerization reaction of pyrrole. The current is quite weak at 0.6V vs. SCE with or without ultrasonic irradiation, indicating that the ultrasonic wave does not affect the reaction mechanism of the polymerization of pyrrole.

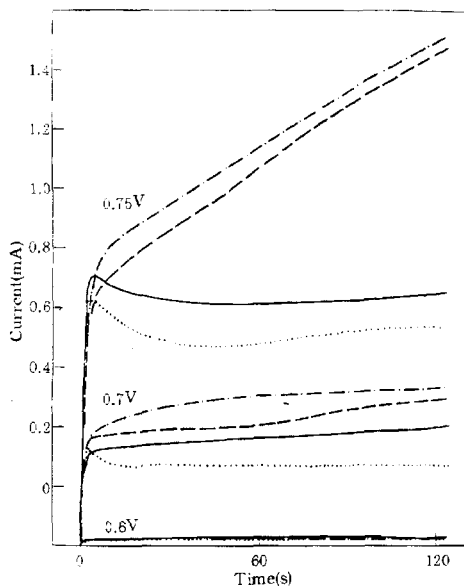


Fig. 1 Chronoamperometric curves of the potentiostatic polymerization of pyrrole
Conditions: pH 3, 0.1mol/L pyrrole, 0.2mol/L TsONa aqueous solution without the irradiation of ultrasonic wave (.....), under the ultrasonic wave of 44W (—), 55W (---) and 66W (- · - · -)

Effect of ultrasonic wave on the conductivity of PPy

The conductivity of the PPy films prepared at different conditions were measured to investigate the effect of ultrasonic field on the polymerization. The results are tabulated in Table 1. Obviously, PPy [44W] which refers to the polypyrrole films produced under the ultrasonic field with the generator power of 44W possesses the highest conductivity for every kind of electrolyte solutions. For the films prepared from the aqueous solutions containing NO_3^- , ClO_4^- or Cl^- , the conductivity of the PPy [44W] films is over 3 times higher than that of PPy [0W] which refers to the polypyrrole films prepared without the irradiation of the ultrasonic wave. However, with further increase of the ultrasonic intensity the conductivity does not enhance further, it turns to decrease contrarily. When the power of the ultrasonic wave

generator reaches 55W, the conductivity of the as-prepared films is lower than that of the unirradiated ones. With the power of 66W it goes even worse. So it can be concluded that the irradiation of the ultrasonic wave with moderate intensity is favourable to preparing highly conductive PPy films. Too strong intensity of the ultrasonic wave deteriorates the as-prepared PPy films and results in the decrease of its conductivity.

Table 1 Conductivity of the polypyrrole films prepared at different conditions

Supporting electrolyte	Conductivity (S cm ⁻¹)					
	PPy[0W]	PPy[44W]	PPy[55W]	PPy[66W]	PPy[77W]	PPy[emuls.]*
TsOH(PC)	61.2	70.2	21.96	2.8		43.5
TsONa	87.6	116.7	80.6	66.8	41.7	94.7
Na ₂ SO ₄	3.2	6.3	2.4	1.2	1.1	5.1
NaNO ₃	6.0	20.2	11.3	5.6	0.8	13.6
NaClO ₄	5.4	24	16.2	4.2	2.9	20.9
NaCl	6.7	23.8	6.4	1.5		16

* PPy[0W]: the PPy films prepared without irradiation of the ultrasonic wave

PPy[44W]: the PPy films prepared under the ultrasonic field of 44W and so on

PPy[emuls.]: the PPy films prepared in the solution pre-emulsified by ultrasonic

Table 2 Tensile strength of the polypyrrole films prepared at different conditions

Supporting electrolyte	Tensile strength (M Pa)				
	PPy[0W]	PPy[44W]	PPy[55W]	PPy[66W]	PPy[emuls]
TsOH(PC)	40.5	72.2	38.0	19.8	53.2
TsONa	27.9	38.5	27.0		
Na ₂ SO ₄	4.56	5.43			
NaNO ₃	2.63	3.27			
NaClO ₄	3.06	5.32			
NaCl	5.79	8.32			

The effect of the ultrasonic wave on the polymerization of pyrrole could be analyzed as the following: The irradiation of ultrasonic wave can produce the effect of emulsification, micro-agitation and cavitation in liquid solutions^[10,11], which have an excellent effect on the homogeneity, hardness and current efficiency on electroplating^[12]. The reaction rate of the electropolymerization of pyrrole is generally considered to be controlled by the diffusion process. Under the ultrasonic wave, the diffusion of pyrrole monomer and solution anions will be enhanced by the micro-agitation. As the solubility of pyrrole in water is poor, the emulsification effect of the ultrasonic will enhance the solubility of pyrrole in the aqueous solution, so as to favor the electropolymerization. That may be the reason why the conductivity of the films obtained in the pre-emulsified aqueous solutions is higher than PPy[0W]

while the emulsification on PC solution has no effect on the conductivity (see Table 1) since the solubility of pyrrole is good in PC. The cavitation effect accompanies with a strong acoustic pressure^[10]. The results mentioned above implies that moderate pressure may favor the growth of highly conductive PPy chain. But too strong cavitation may result in the degradation of the polymer^[11] and destroy the deposited PPy films. The power of 44W of the ultrasonic generator used in this work is the threshold for producing cavitation in the solutions. So it can be assumed that the weakest cavitation is favourable to the polymerization of pyrrole.

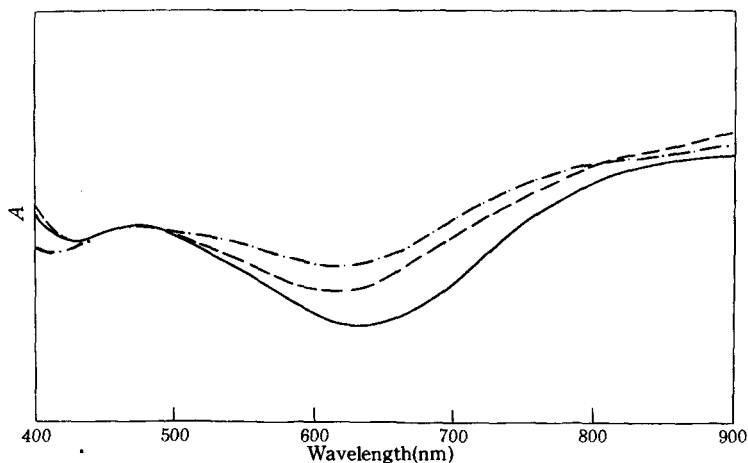


Fig. 2 Visible absorption spectra of PPy[0W] (—), PPy[44W] (---) and PPy[66W] (- · - · -)

Effect of ultrasonic wave on the tensile strength of PPy

The effect of ultrasonic wave on the tensile strength of the PPy films, as shown in Table 2, is the same as that on the conductivity discussed above. For the films produced in PC solutions, the tensile strength of PPy[44W] is 72.2 MPa which is 80% higher than that of PPy[0W]. The order in the magnitude of the tensile strength is: PPy[44W] > PPy[emuls.] > PPy[0W] > PPy[55W] > PPy[66W]. For the films produced in aqueous solutions, the tensile strength of PPy[44W] is also higher than that of PPy[0W]. So, the irradiation of the moderate ultrasonic wave favors the preparation of flexible PPy films too.

Effect of ultrasonic wave on the absorption spectra of PPy

In order to investigate the structural characteristics of the PPy films produced under the irradiation of ultrasonic wave, the visible absorption spectra were measured. Fig.2 shows the absorption spectra of the PPy films prepared on ITO electrode in the aqueous solutions containing 0.2mol/ml NaNO_3 . The absorbance of

PPy[44W] from 600 to 900nm increased obviously compared with that of PPy[0W], indicating that the doping concentration of PPy[44W] is higher than that of PPy[0W]. The absorption of PPy[77W] dropped at the wavelength longer than 700nm, probably resulted from the degradation of the PPy films.

The electrochemical reduction of PPy(NO_3^-) in acidic aqueous NaNO_3 solution is accompanied with the de-doping of counter-anion NO_3^- [13]. The charge consumed in the reduction corresponding to the quantity of counter-anions doped in the films. Fig.3 shows the cyclic voltammograms of PPy[0W], PPy[44W] and PPy[77W] prepared in aqueous NO_3^- solutions with a polymerization charge of 10mC. The reduction current of PPy[44W] is larger than that of PPy[0W] in the whole potential range from 0.2V to -0.8V vs. SCE, indicating that the doping amount of counter-anions in PPy[44W] is higher than that in PPy[0W]. This result agrees with the absorption spectra mentioned above.

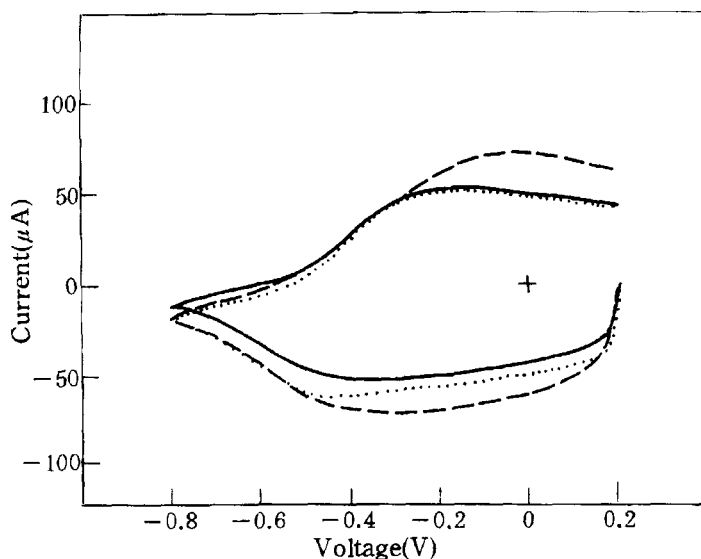


Fig. 3 Cyclic voltammograms of NO_3^- -doped PPy[0W] (—), PPy[44W] (.....) and PPy[66W] (---) in pH 3, 0.2mol/L NaNO_3 aqueous solution with the potential scan rate of 20mV/s

CONCLUSION

The effect of ultrasonic wave on the electropolymerization of pyrrole was studied by potentiostatic polymerization, conductivity and tensile strength measurement, visible absorption spectrometry and cyclic votammetry, etc. It was found that the polypyrrole films prepared under moderate ultrasonic irradiation possesses higher

conductivity, better tensile strength and higher doping degree of the counter-anions. Too strong ultrasonic intensity destroys the PPy chain structure and deteriorates the quality of the prepared films.

Keywords:

Polypyrrole; Electropolymerization; Ultrasonic wave; Tensile strength; Conductivity

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