

## CHAPTER III

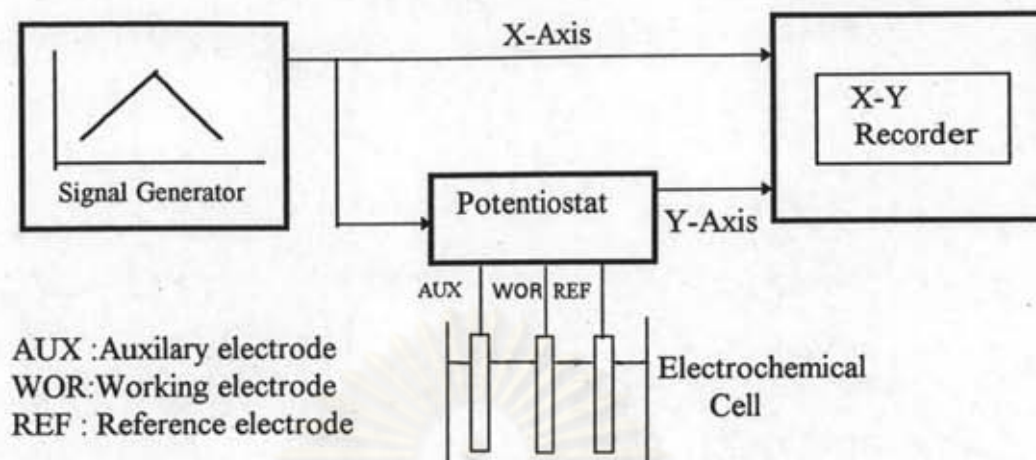
### CYCLIC VOLTAMMETRY OF POLYPYRROLE SYNTHESIZED BY ELECTROCHEMICAL AND CHEMICAL METHODS

#### Introduction

It was known that electrochemically synthesized polypyrrole (Eppy) can be very well used as an electrode of rechargeable battery [2]. In this work it is aimed to investigate the possibility of using chemically synthesized polypyrrole (Cppy), which prepared by a different method, as an electrode of rechargeable battery. The first investigation is to study cyclic voltammogram of this Cppy. This experiment will reveal whether the doped and undoped processes of Cppy can be performed and for how many cycles. The ability in performing this electrochemical reaction is basic requirement for a good electrode of rechargeable battery.

#### Instrumentation

Cyclic voltammogram was carried out using the instruments set up in Figure 3.1. They consisted of a signal generator (612 VA Scanner, Metrohm), a potentiostat (626 Polarcord, Metrohm), X-Y recorder (Graphic Corporation) and electrochemical cell.



**Figure 3.1** Block diagram of instruments for cyclic voltammetry

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## Reagents

Reagents used in the experiments are listed below:

1. Platinum metal	Aldrich
2. Propylene carbonate	Fluka
3. Tetrabutylammoniumperchlorate	Fluka
4. Methanol	J.T.Baker
5. Anhydrous Ferric chloride	Fluka
6. Anhydrous Calcium chloride	Fluka
7. Potassiumthiocyanate	Fluka
8. Nitrogen gas, 99.999 % purity	TIG
9. Pyrrole	Fluka

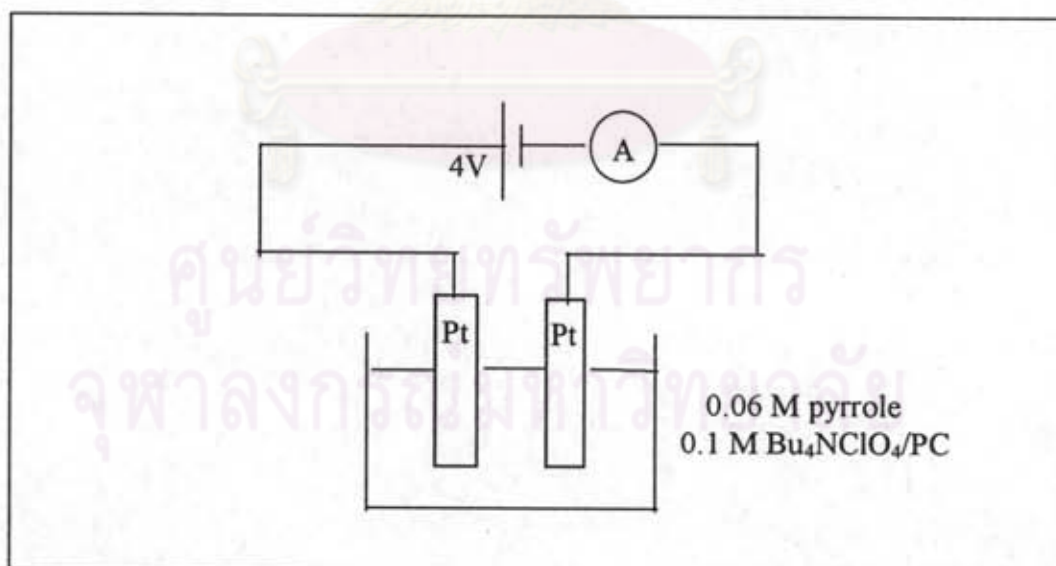
(Pyrrole monomer was distilled under reduced pressure. The distillate was collected and stored under a nitrogen atmosphere in refrigerator )

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## Experimental

### Polypyrrole from Electrochemical Synthesis

Polypyrrole synthesized by electrochemical method could be performed in the one-compartment electrochemical cell [15] illustrated in Figure 3.2. The cell consisted of two platinum electrodes and contained 0.06 M pyrrole, 0.1 M tetrabutylammoniumperchlorate ( $\text{Bu}_4\text{NClO}_4$ ) in propylene carbonate (PC). The electrochemical polymerization could be carried out by using 4 V power supply. The darkening of the platinum electrode could be observed when polypyrrole film gradually deposited on electrode surface. Since the film thickness increased with reaction time, the thin or thick films could then be prepared by controlling the reaction time and the current supplied.

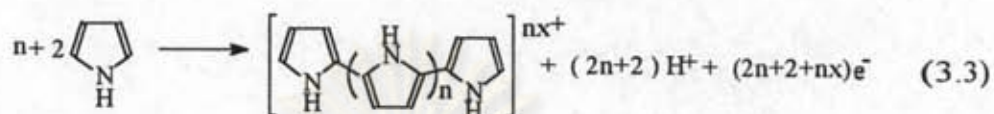
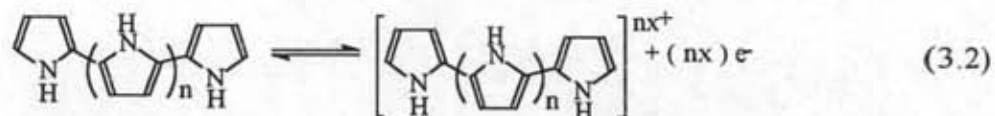
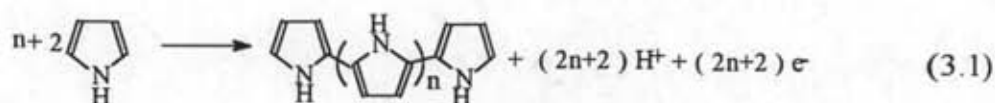


**Figure 3.2** The one-compartment electrochemical cell for the synthesis of polypyrrole

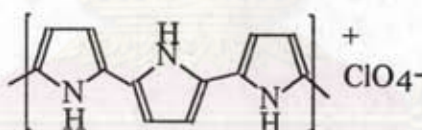
**Table 3.1** The electrochemical cell current of polypyrrole synthesis

Time (min)	I (mA)
0	4.36
2	4.36
4	4.35
6	4.35
8	4.35
10	4.34
12	4.34
14	4.34
16	4.34
18	4.34
20	4.34

Table 3.1 showed typical electrochemical cell current in the synthesis. The current was almost constant with reaction time, it indicated that the film being deposited on positive electrode at constant rate and this film is conductive. The polypyrrole showed high electrical conductivity of is approximately  $10^2 \text{ Scm}^{-1}$ [16]. The stoichiometry of the reaction was shown in Equation 3.3.



The apparent stoichiometry included the stoichiometry for the formation of the polymer chain, which is 2.0 for large values of  $n$  (Equation 3.1), plus the charge associated with oxidation of the polymer (Equation 3.2). The level of oxidation of polypyrrole contained perchlorate counterion was 0.30 per pyrrole unit, corresponding to one anion for every 3 units of pyrrole, in this case  $x = 1/3$ . The structure of polypyrrole was shown in Figure 3.3 [9-10].



**Figure 3.3** Structure of polypyrrole synthesized by electrochemical method

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### Polypyrrole from Chemical Synthesis

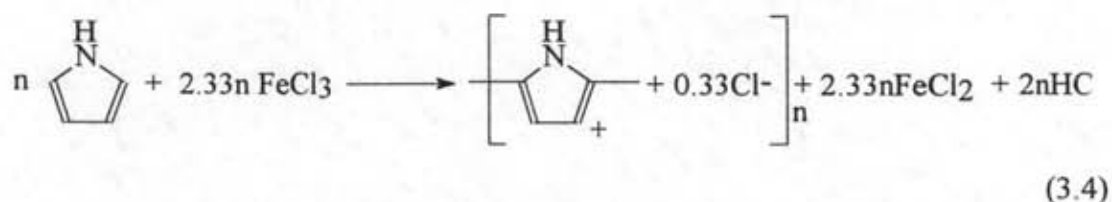
It was found that polypyrrole could be simply prepared by the oxidation of pyrrole with ferric chloride ( $\text{FeCl}_3$ ) in methanol solution ([17]. The experimental is proceeded as follows.

Ferric chloride solution in methanol was added into three-neck glass reactor equipped with a mechanical stirrer, gas inlet tube for bubbling the nitrogen, calcium chloride tube and a septum. Nitrogen gas was passed through  $\text{FeCl}_3$  solution at  $0^\circ\text{C}$  for 1 hour. After that the polymerization was started by injecting a pyrrole monomer through the septum by syringe into the solution with continuous stirring. A black powder formed almost instantaneously, and as the reaction progressed the color of the solution turned from rusty orange to green. The polymerization reaction was quenched by adding copious amount of methanol in order to dilute  $\text{FeCl}_3$  solution. Then polymer powder was filtered and washed with methanol until the filtrate was colorless and contained no  $\text{Fe(III)}$ , as indicated by testing with potassiumthiocyanate. The polymer powder was then washed with acetone and vacuum dried in the desiccator at room temperature.

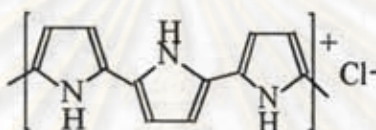
The most suitable polymerization condition for the synthesis of polypyrrole with the highest electrical conductivity when a 1 ml pyrrole monomer is used, was as follows [17]:

conductivity	: $10^2 \text{ Scm}^{-1}$
concentration of $\text{FeCl}_3$	: 2.5 M
reaction time	: 20 min
reaction temperature	: $0^\circ\text{C}$

The net reaction of pyrrole with  $\text{FeCl}_3$  in Equation 3.4 was considered.



From this reaction one chlorine atom accepted one electron from three pyrrole monomer units to become a dopant anion. Possible structure of polypyrrole synthesized in this method was shown in Figure 3.4.



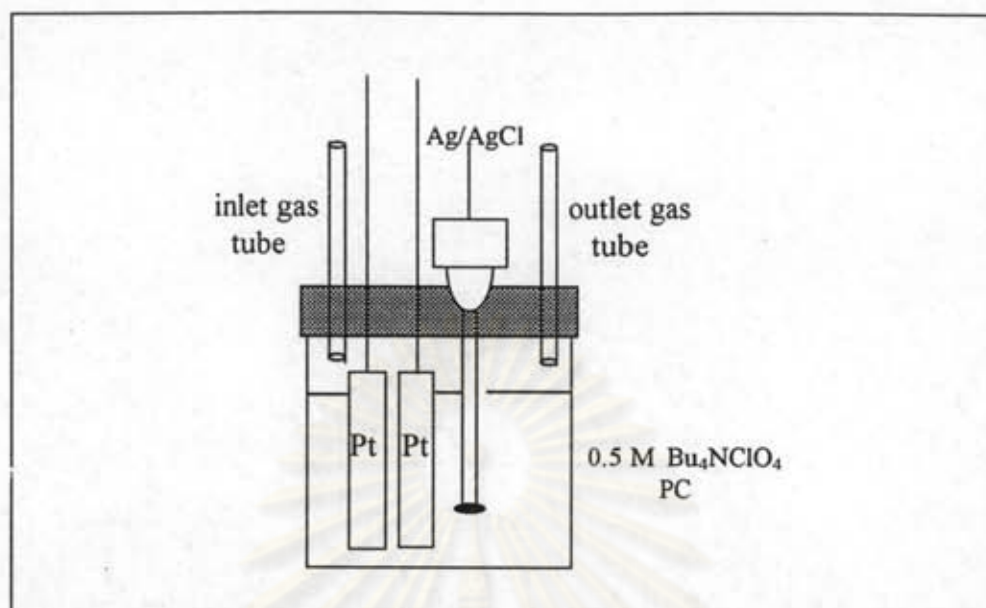
**Figure 3.4** Possible structure of polypyrrole synthesized by chemical method

### Cyclic Voltammetry of Electrolyte Blank with Platinum Electrode

Cyclic voltammetry of electrolyte blank with platinum electrode was carried out for testing background current to compare with the current occurred from cyclic voltammetry of Cppy and Eppy. Procedure for cyclic voltammetric measurement of electrolyte blank proceeds as follows.

Two clean platinum plates were mounted as working and auxiliary electrodes in the electrochemical cell illustrated in Figure 3.5 using Ag/AgCl reference electrode. Electrolyte solution was a 1 M  $\text{Bu}_4\text{NClO}_4$  in PC. During this experiment, nitrogen gas was continuously passed through the electrochemical cell. Cyclic voltammetric measurement of blank solution was started after nitrogen gas passed through this cell for 30 min.

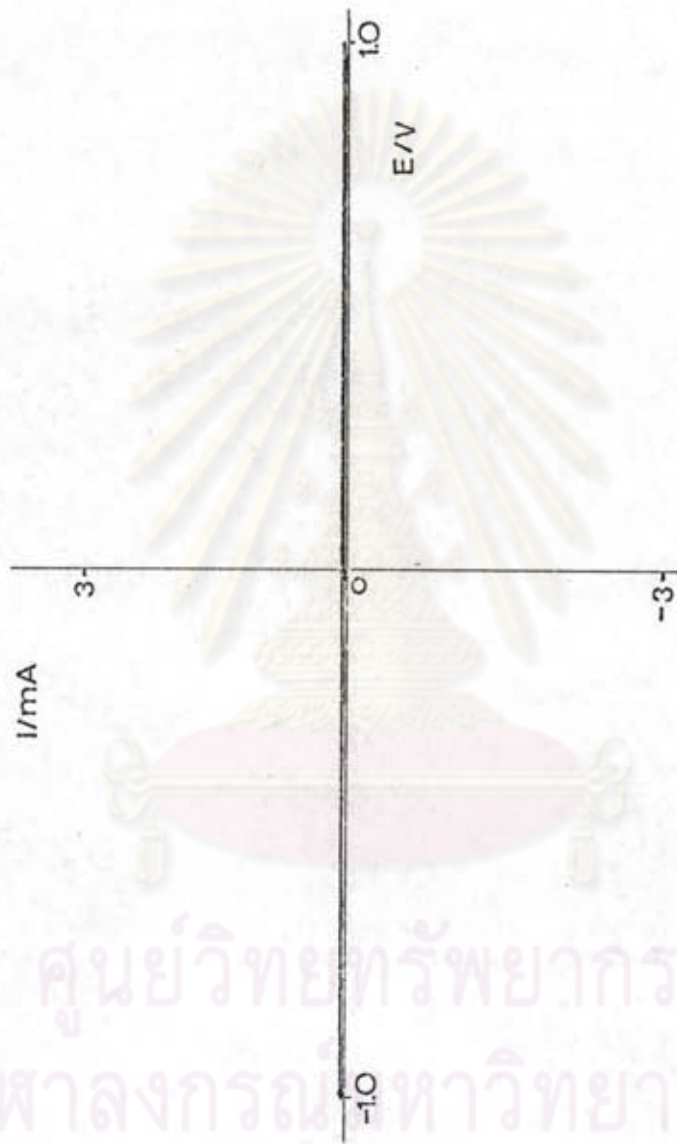




**Figure 3.5** Electrochemical cell for cyclic voltammetric measurement of the electrolyte blank.

When the experiment was started, the instrument produced the potential between working and auxiliary electrodes changing with time for making the potential between working vs. reference electrodes was varied. The result was shown as the cyclic voltammogram in Figure 3.6, it indicated that when the potential between working and reference electrodes was varied linearly from -1.0 up to 1.0 V and down to -1.0 V of the various sweep rates, it was found that the current was zero. This means the electrochemical reaction was not occurred.

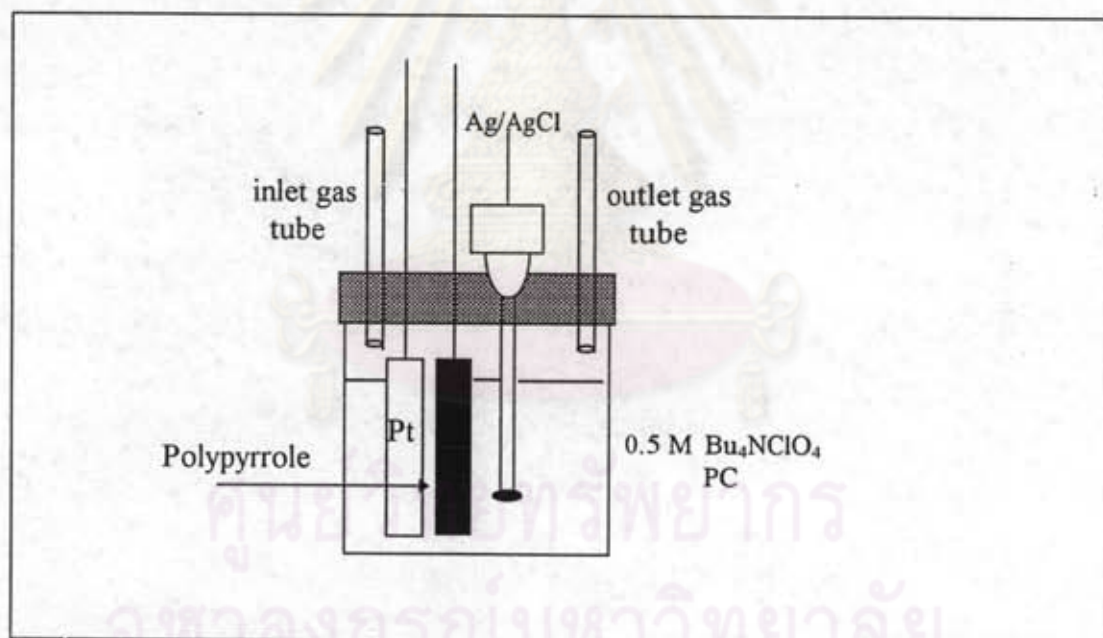
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**Figure 3.6** Cyclic voltammogram of electrolyte blank with platinum electrode measured in a 1 M  $\text{Bu}_4\text{NClO}_4$  in PC using Ag/AgCl reference electrode with various sweep rates.

### Cyclic Voltammetry of Electrochemically Synthesized Polypyrrole

Polypyrrole was electrochemically polymerized with reaction time of 10 sec in thin film of about 20 nm thick on platinum electrode. After the polymerization, polypyrrole was rinsed with PC and mounted as working electrode in electrochemical cell illustrated in Figure 3.7 using platinum plate as auxiliary electrode and Ag/AgCl reference electrode. Electrolyte solution was a 0.5 M  $\text{Bu}_4\text{NClO}_4$  in PC. During this experiment, nitrogen gas was continuously passed through the electrochemical cell. Cyclic voltammetric measurement was started after nitrogen gas passed through this cell for 30 min.

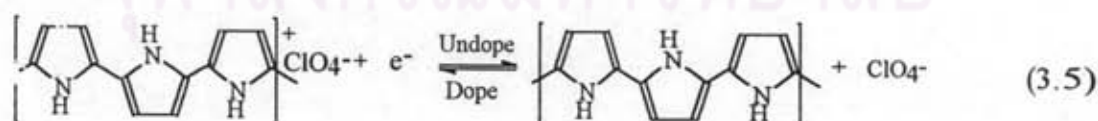


**Figure 3.7** The electrochemical cell for cyclic voltammetric measurement of Eppy.

**Table 3.2** The electrochemical cell current of polypyrrole synthesis

Time (sec)	I (mA)
0	4.22
1	4.22
2	4.22
3	4.21
4	4.21
5	4.20

Cyclic voltammetric measurement of polypyrrole with thickness of 20 nm was recorded. The doped and undoped processes on anodic and cathodic sweep can be repeatedly induced as shown in Figure 3.8, it indicated that electrochemical reactions could be carried out in this measurement. When the potential between working and reference electrodes varied linearly from -1.3 up to 0.8 V and then down to -1.3 V with a sweep rate of  $100 \text{ mVs}^{-1}$ , an oxidation peak of polypyrrole film at 0.15 V on the anodic sweep and a reduction peak at -0.02 V on the cathodic sweep appeared. The redox reaction accompanied by a movement of the perchlorate anion ( $\text{ClO}_4^-$ ) in and out of the film was shown in the Equation 3.5.



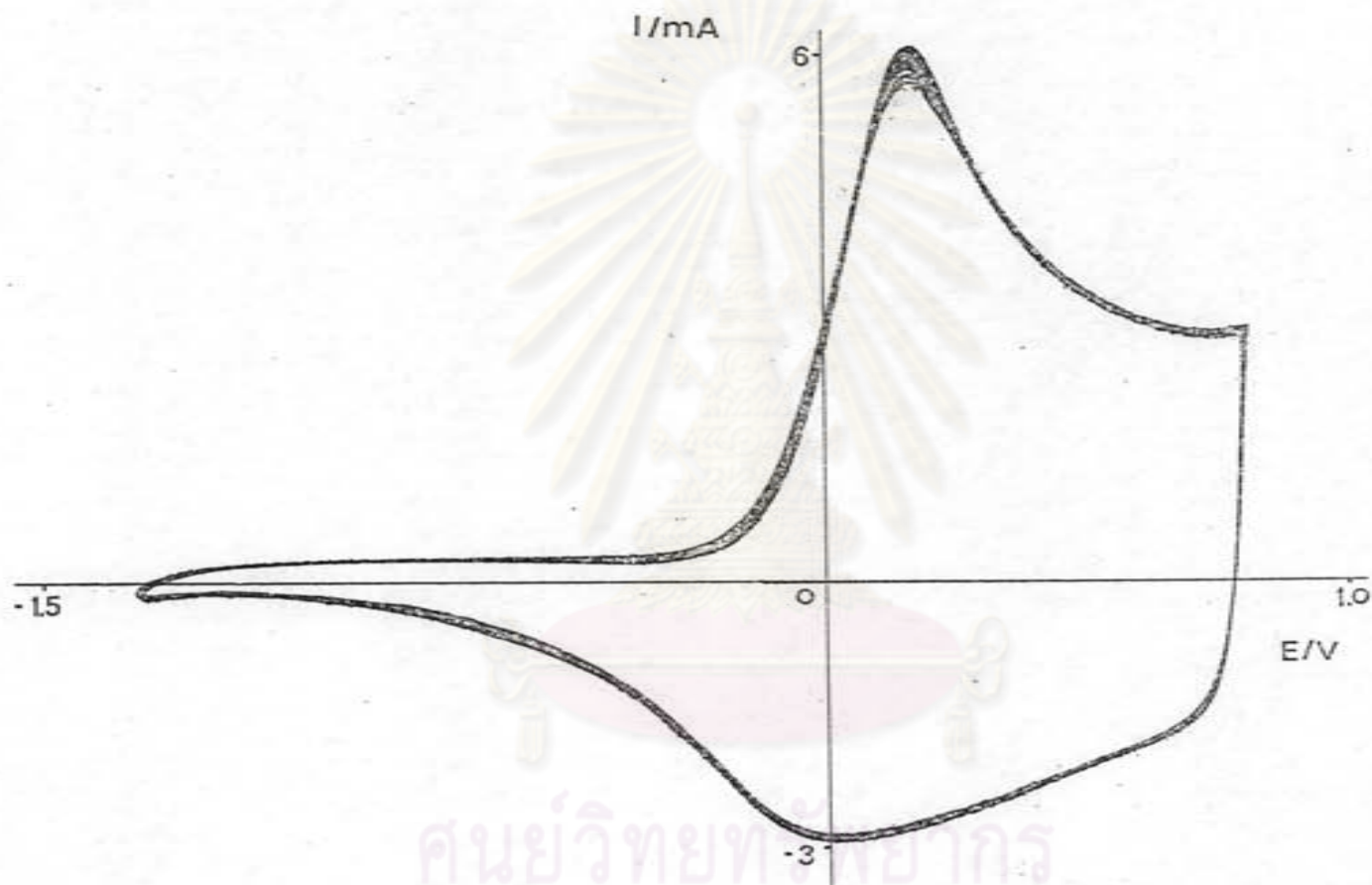
Conducting form

Nonconducting form

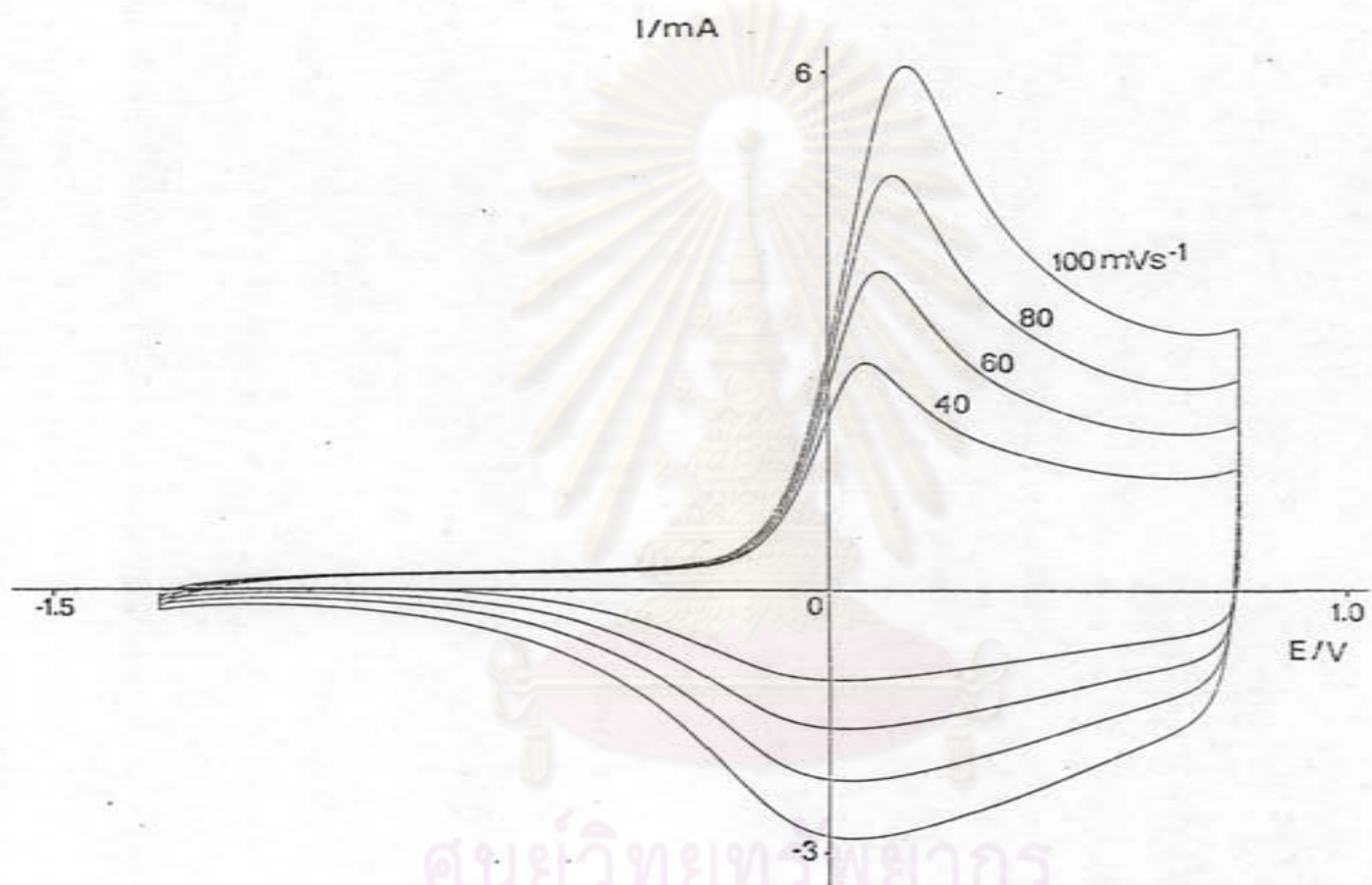
From the equation 3.5, the redox reaction involved doped and undoped processes of polypyrrole film. When the potential of working electrode was negative compared with the auxiliary electrode, the  $\text{ClO}_4^-$  was released from Eppy to electrolyte and conducting Eppy was changed to insulator. This could be observed from very small current on the left side of Figure 3.8. When the potential of the electrode was swept to positive side, the doped process or oxidation reaction of Eppy occurred. The  $\text{ClO}_4^-$  moved from the electrolyte to associate with Eppy. The insulating form of Eppy changed to the conducting form and the current was increased.

During the multiple sweep, the current in the first cycle of the potential sweep was small. This means that only small percentage of  $\text{ClO}_4^-$  was released from polypyrrole and encountered into polypyrrole in the cathodic sweep and anodic sweep, respectively. In other words the redox process was incomplete at the beginning.

In other sweep rates, the result obtained from cyclic voltammogram in Figure 3.9 showed asymmetrical waves. At the faster sweep rate, the peak current occurred at higher potential since the in and out movement of these  $\text{ClO}_4^-$  situated deeper in electrode was rather difficult compared to those located near the surface. Moreover, when Eppy was doped and undoped with faster sweep rate, the quantity of  $\text{ClO}_4^-$  cooperated in this process was smaller. The undoped process was incompleting in rather fast sweep rate as observed by a small current remained on the left side of Figure 3.9.



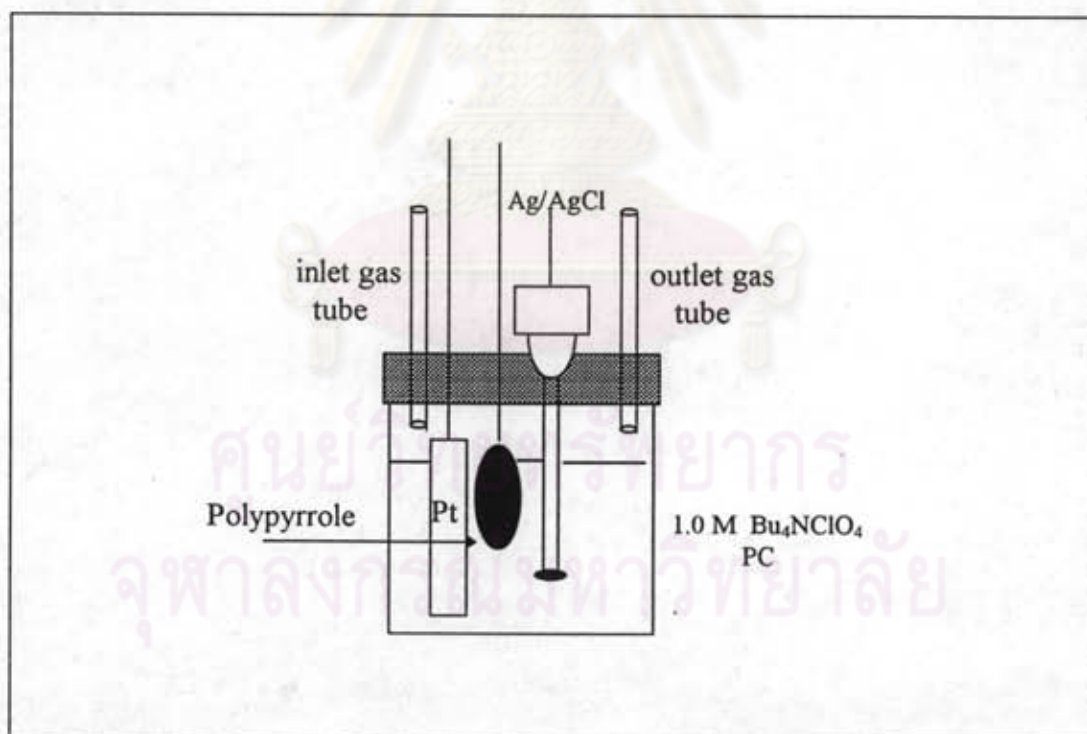
**Figure 3.8** Cyclic voltammogram of electrochemically synthesized polypyrrole film measured in a 0.5 M  $\text{Bu}_4\text{NClO}_4$  in PC using Ag/AgCl reference electrode with a sweep rate of  $100 \text{ mVs}^{-1}$ .



**Figure 3.9** Cyclic voltammogram of electrochemically synthesized polypyrrole film measured in a 0.5 M  $\text{Bu}_4\text{NClO}_4$  in PC using Ag/AgCl reference electrode with various sweep rates.

### Cyclic Voltammetry of Chemically Synthesized Polypyrrole

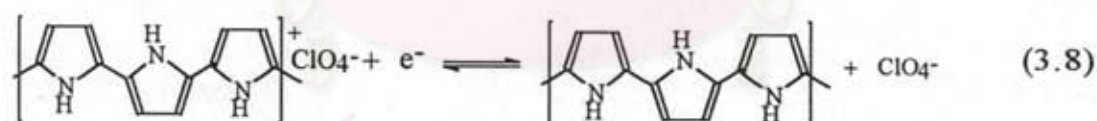
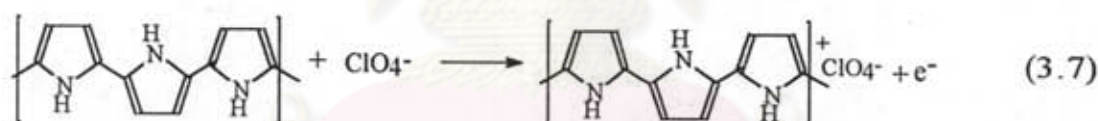
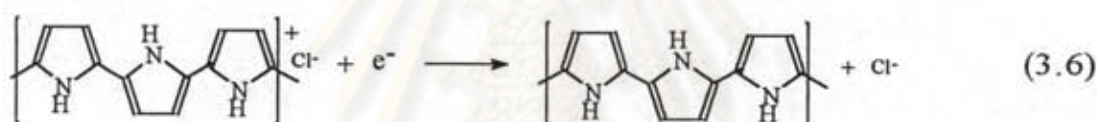
Polypyrrole powder was transformed into a thin disc by pressing under two tons of hydraulic force in evacuable die for 10 minutes ( $\Phi = 1.2$  cm, thickness = 0.15 mm). After that the polypyrrole sample was mounted as working electrode in the electrochemical cell illustrated in Figure 3.10, using platinum plate as auxiliary electrode and Ag/AgCl reference electrode. Electrolyte solution was a 1 M  $\text{Bu}_4\text{NClO}_4$  in PC. During this experiment, nitrogen gas was continuously passed through the electrochemical cell. Cyclic voltammetric measurement was started after passing nitrogen gas through this cell for 30 minutes.



**Figure 3.10** Electrochemical cell for cyclic voltammetric measurement of Cppy



Cyclic voltammetric measurement of polypyrrole synthesized from chemical method was measured. The result showed by cyclic voltammogram in Figure 3.11 indicated that some electrochemical reactions were occurred in this measurement. When the potential between working electrode and reference electrode varied linearly from -1.0 up to 0.8 V and down to -1.0 V with sweep rate of  $10 \text{ mVs}^{-1}$ , the oxidation peak of polypyrrole film occurred at 0.25 V on the anodic sweep. In the cathodic sweep, the reduction peak at -0.35 V appeared. The early redox reaction accompanied mainly by the movement of the anions  $\text{ClO}_4^-$  and chloride ( $\text{Cl}^-$ ) out of polypyrrole disc in order to compensate the cationic charge in the oxidized polymer. Later nearly all  $\text{ClO}_4^-$  probably participated in the redox process. These reactions were shown in Equations 3.6-3.8.



From the equation 3.6, the redox reaction involved doped and undoped processes of polypyrrole. When the potential of working electrode was appreciably negative compared with auxiliary electrode,  $\text{Cl}^-$  was released from Cppy. The conducting form of Cppy was changed to insulator, it could be observed from the very small current on the left side of Figure 3.11. When the potential increased, the doped process or oxidation reaction of Cppy was occurred. Large quantity of  $\text{ClO}_4^-$  and some small quantity of  $\text{Cl}^-$  moved from the electrolyte into Cppy. The insulating form changed to the conducting form, the current was

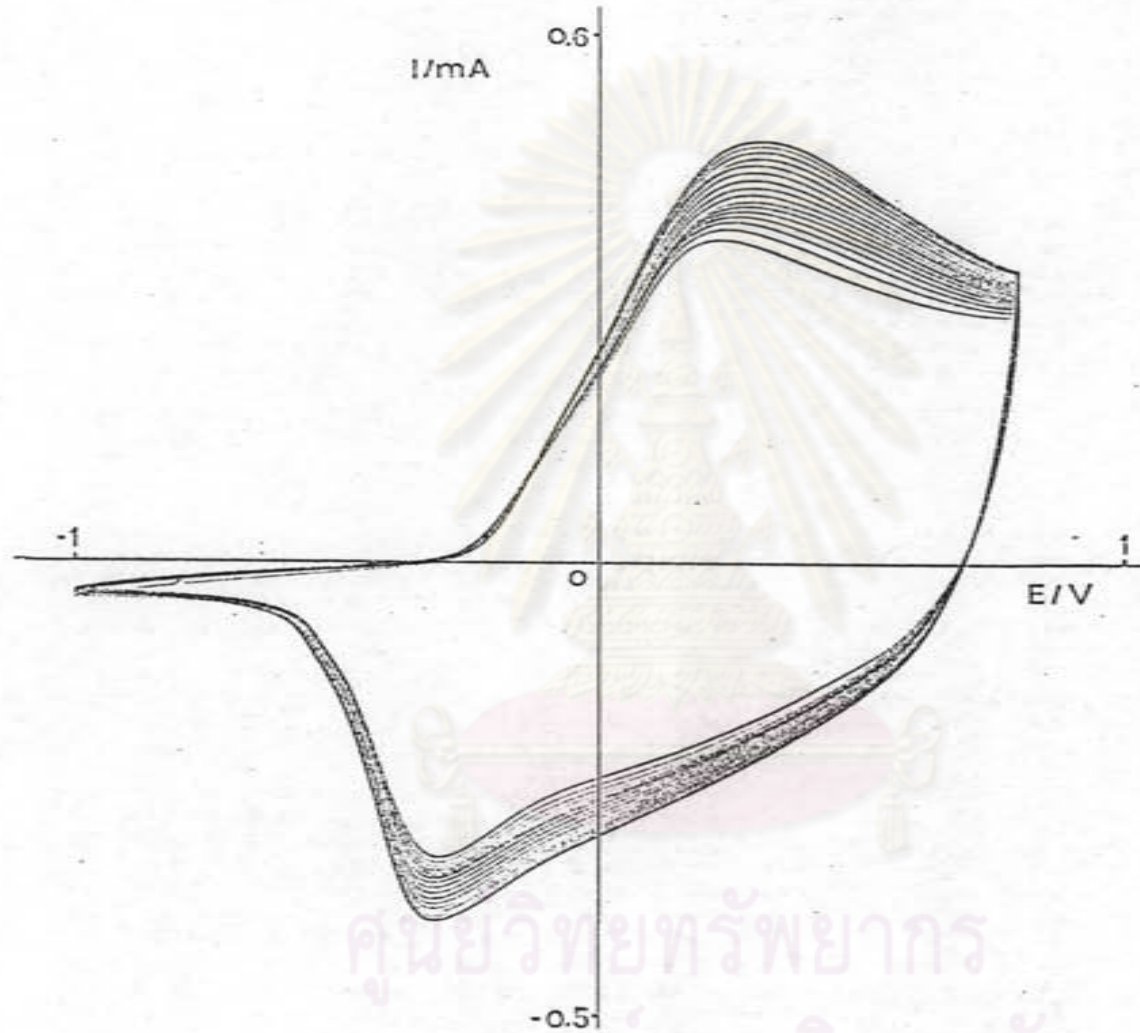


Figure 3.11 Cyclic voltammogram of chemically synthesized polypyrrole measured in a 1 M  $\text{Bu}_4\text{NClO}_4$  in PC using Ag/AgCl reference electrode with a sweep rate of  $10 \text{ mVs}^{-1}$ .

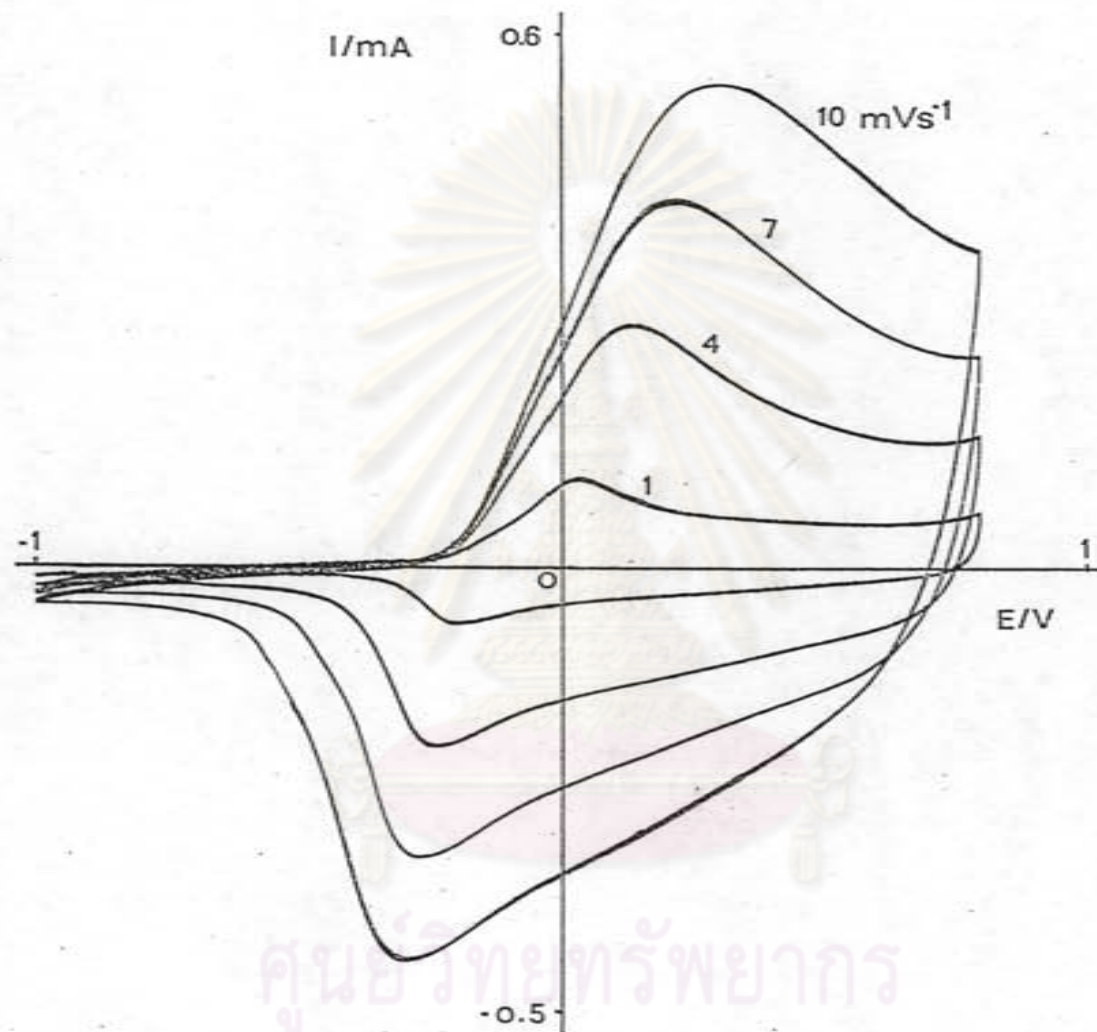


Figure 3.12 Cyclic voltammogram of chemically synthesized polypyrrole measured in a 1 M  $\text{Bu}_4\text{NClO}_4$  in PC using Ag/AgCl reference electrode with various sweep rates

increased. When the potential was decreased again, the current was then negative since the undoped process or reduction reaction of Cppy occurred. The  $\text{ClO}_4^-$  and  $\text{Cl}^-$  were released from Cppy to electrolyte. The conducting form changed again to the insulating form, and so on. During the multiple sweep, the I-V loop was gradually enlarged. This indicated that at early state the doped and undoped processes were rather difficult to induce.

With the various sweep rates, the result obtained from cyclic voltammogram in Figure 3.12 showed asymmetrical waves. At the faster sweep rate, the peak current occurred at higher potential since it is more difficult for inner  $\text{ClO}_4^-$  or  $\text{Cl}^-$  to move in and out between electrode and electrolyte. Moreover, when Cppy was undoped with faster sweep rate, the quantity of  $\text{ClO}_4^-$  and  $\text{Cl}^-$  released was smaller. The undoped process was incompleated as was observed from the small current on the left side of the Figure 3.12.

## Conclusion

For the study of polypyrrole synthesized from chemical method as electrode material by using cyclic voltammetric technique, it is found that the chemically synthesized polypyrrole showed more symmetrical cyclic voltammogram which indicated that its electrode reaction showed better reversibility than the electrode reaction of electrochemically synthesized polypyrrole. However, both polypyrrole showed similarly good electrode properties. They can be repeatedly driven between nonconducting and conducting states by doped and undoped processes without loss of activity. The application of polypyrrole synthesized from chemical method as electrode material in rechargeable battery is possible.