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"IMPROVED PROCESS FOR ELECTROCHEMICAL SYNTHESIS OF POLYPYRROLE".

The following specification describes the nature of this invention.

PRICE: TWO RUPEES
161055

This is an invention by Dinesh Chandra Trivedi, Venkata Subramanian Krishnan, Kodethoor Shrivara Udupa and Kummattithidal Santhanam Rajagopalan, Scientists of Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, all Indian Citizens.

The invention relates to the electrochemical preparation of polypyrrole from pyrrole in an electrolyte of either acetonitrile or dimethyl formamide containing either anhydrous sodium perchlorate or lithium perchlorate, using stainless steel as the anode and the cathode.

This conducting polymer of polypyrrole can be used as an anode and cathode material in high energy density organic battery. They also find a place in storage of electronic components such as IC Chips. This polymerisation could be carried out either in an undivided cell or in a divided cell.

Hitherto the electrochemical polymerisation of pyrrole and the subsequent preparation of polypyrrole was done on anodes such as Pt, Au, SnO₂ and In₂O₃, in an Argon atmosphere.

The chemical method of polymerisation of pyrrole leads to the formation of polymer of very low conductivity (≈ 10⁻⁹ to 10⁻⁷ ohm⁻¹ cm⁻¹). Moreover various side products of pyrrole are also formed during the chemical reaction which cannot be avoided.
Hence the main object of this invention is to develop an electrochemical method for the preparation of polypyrrole without any side products having high conductivity.

To these ends, the invention broadly consists of the following details. In a 200 ml glass beaker a stainless steel cathode and an anode of either a platinum or nickel or stainless steel were fixed at an inter electrode distance of 1-3 cm. Anhydrous sodium perchlorate of strength 0.1M = 1M or Lithium perchlorate of strength 0.1M =1M was used as the electrolyte in either acetonitrile (100 ml) or dimethyl formamide (100 ml) or tetrahydrofuran (100 ml). All experiments were carried out in anhydrous condition under the nitrogen atmosphere. The water content of the medium is 10^-2 mole 1^-1. Even traces of oxygen leads to polymers of low conductance. Other solvents such as CH₂Cl₂ and supporting electrolyte such as N(Bu)₄BF₄ can be used. A current of 0.02 to 0.5 amperes (cd= 0.001A/cm² to 0.012A/cm²) depending on the anode area was passed. For a charge density of 24 mc/cm² the thickness is 1 micron. This polymer black in colour, is highly insoluble in common organic solvents. The faradaic yield for conversion has been calculated to be about 0.45 to 0.55 molar per mole of electrons. The anode potential during electrolysis is 0.8V vs SCE and this is maintained.

The oxidation potential of monomer pyrrole remains unchanged with different solvents and supporting electrolytes indicating an uniform polymer formation on the anode surface. At an anode potential of 0.8V vs SCE the current increases sharply and gets stabilised after a few minutes. On passing the current the anode
Surface becomes black due to polypyrrole formation. The conductance of polymer allows the fast growth of a film of many micrometer thickness. The conductivity was measured by a four-point probe technique and the conductivity ($\sigma$) of polypyrrole was found to be $0.5 \text{ to } 10 \ \text{cm}^{-1} \text{ cm}^{-1}$. The conducting polymer thus formed is adhesive on the anode surface and it can be easily peeled off after building up sufficient thickness (1 micron). This polymer is quite stable up to $150^\circ \text{C}$.

A plurality of examples are given below to illustrate the invention:

**Example 1**

**Supporting electrolyte**: Anhydrous sodium perchlorate (1M) in 100 ml of acetonitrile (double distilled). The electrolyte was deaerated by passing nitrogen.

**Pyrrole**: 0.1M

**Anode area**: Stainless steel of 30 cm$^2$ area

**Cathode area**: Stainless steel of 30 cm$^2$ area

**Temperature**: Room Temperature ($30\text{ to }35^\circ \text{C}$)

**C.d. employed**: 0.006A/cm$^2$

**Cell voltage**: 2.4V

**Duration of electrolysis**: 30 minutes

**Thickness obtained**: 0.1 mm

**C.E.**: 55%

**Conductivity**: $1.5 \ \text{ohm}^{-1} \text{ cm}^{-1}$
Example 2

Supporting electrolyte: Anhydrous lithium perchlorate (1M) in 100 ml of acetonitrile (Double distilled). The electrolyte was deaerated by passing nitrogen.

Pyrrole: 0.1 M

Anode area: Stainless steel of 30 cm² area

Cathode area: Stainless steel of 30 cm² area

Temperature: Room Temperature (30-35°C)

Cell voltage: 4.5 V

Current Density: 0.006 A/cm²

Duration of electrolysis: 30 minutes

Thickness obtained: 0.1 mm

C.E.: 55%

Conductivity: 1.8 Ω cm⁻¹

Example 3

Supporting electrolyte: Anhydrous sodium perchlorate (1M) in 100 ml dimethyl formamide (Double distilled). The electrolyte was deaerated by passing nitrogen.

Pyrrole: 0.1 M

Anode area: Stainless steel of 30 cm² area

Cathode area: Stainless steel of 30 cm² area

Temperature: Room temperature (30-35°C)

C.d. employed: 0.006 A/cm²

Cell voltage: 4.5 V

Thickness obtained: 0.2 mm

C.E.: 55%

Conductivity: 0.8 Ω cm⁻¹
Example 4

Supporting electrolyte: Anhydrous lithium perchlorate (1M) in 100 ml dimethyl formamide (Double distilled). The electrolyte was deaerated by passing nitrogen.

Pyrrole: 0.1 M

Anode area: Stainless steel of 30 cm² area

Cathode area: Stainless steel of 30 cm² area

Temperature: Room Temperature (30-35°C)

C.d. employed: 0.006A/cm²

Cell voltage: 4.5 V

Duration of electrolysis: 30 minutes

Thickness obtained: 0.2 mm

C.E.: 55%

Conductivity: 0.8 ohm⁻¹ cm⁻¹
Example 5

Supporting electrolyte: Anhydrous lithium perchlorate (1 M) in 100 ml dimethyl formamide (Double distilled). The electrolyte was deaerated by passing nitrogen.

Pyrrole: 0.1 M
Anode area: Stainless steel of 30 cm\(^2\) area
Cathode area: Stainless steel of 30 cm\(^2\) area
Temperature: Room Temperature (30-35°C)
C.d. employed: 0.006A/cm\(^2\)
Cell voltage: 5.0 V
Duration of electrolysis: 30 minutes
Thickenss obtained: 0.1 mm
C.E.: 55%
Conductivity: 0.9 ohm\(^{-1}\) cm\(^{-1}\)

Dated this 9th day of July 1984

(SUSHIL KUMAR)
ASSISTANT PATENTS OFFICER
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
COMPLETE SPECIFICATION

(Section—10)

"IMPROVED PROCESS FOR ELECTROCHEMICAL SYNTHESIS OF POLYPYRROLE".

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH Rafi Marg, New Delhi-110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:
This invention is developed by Dinesh Chandra Trivedi, Venkatasubramanian Krishnan, Kodethoor Shrivara Udupa and Kummatthidial Santhanam Rajagopalan, Scientists of Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, all Indian citizens and relates to an improved process for electrochemical synthesis of Polypyrrole.

This polymer of pyrrole can be used as an electrode material in high energy density organic batteries and also find place in storage of electronic components such as IC chips.

Hitherto the electrochemical polymerisation of pyrrole was done on anodes such as Pt, Au, SnO₂ and In₂O₃, in an Argon atmosphere.

The chemical method of polymerisation of pyrrole leads to the formation of polymer of very low conductivity ($\approx 10^{-9}$ to $10^{-7}$ ohm $^{-1}$ cm $^{-1}$). Moreover various side products of pyrrole are also formed during the chemical reaction which cannot be avoided.

Hence the main object of this invention is to develop an electrochemical method for the preparation of polypyrrole without any side products and having high conductivity.

The invention relates to the electrochemical preparation of polypyrrole from pyrrole in an electrolyte containing a supporting electrolyte in a solvent, wherein the anode and the cathode being stainless steel and having an area of 30cm$^2$. 


by way of supporting electrolyte, anhydrous sodium perchlorate and lithium perchlorate may be employed. The examples of the solvents which can be employed it may be mentioned acetonitrile and dimethyl formamide, tetrahydro furan.

An embodiment of the invention is described below with reference to the flow sheet shown in the drawings accompanying this specification.

The invention broadly consists of the following details. In a 200 ml glass beaker a stainless steel cathode and an anode of stainless steel were fixed at an inter electrode distance of 4-3 cm. Anhydrous sodium perchlorate of strength .3M - .5M or lithium perchlorate of strength .4M - .5M was used as the electrolyte in either acetonitrile (100 ml) or dimethyl formamide (100 ml) or tetrahydrofuran (100 ml). The experiment was carried out in anhydrous condition under the nitrogen atmosphere. The water content of the medium is 10⁻² mole l⁻¹. Even traces of oxygen leads to polymers of low conductance. Other solvents such as CH₂C₂ and supporting electrolyte such as N(Bu)₄BF₄ can be used. A current of 0.02 to 0.5 amperes (cd= 0.001 A/cm² to 0.02 A/cm²) was passed. For a charge density of 24 mc/cm² the thickness is 1 micron. This polymer black in colour, is highly soluble in common organic solvents. The faradaic yield for conversion has been calculated to be about 0.45 to 0.55 molar per mole of electrons. The anode potential during electrolysis is 0.8 V vs SCE and this is maintained.
The oxidation potential of monomer pyrrole remains unchanged with different solvents and supporting electrolytes indicating an uniform polymer formation on the anode surface. At an anode potential of 0.8V vs SCE the current increases sharply and gets stabilised after a few minutes. On passing the current the anode surface becomes black due to polypyrrole formation. The conductance of polymer allows the fast growth of a film of many micro meters thickness. The conductivity was measured by Four point probe technique and the conductivity \( \sigma \) of polypyrrole was found to be 0.5 to \( 10^{-7} \) cm \(^{-1}\). The conducting polymer thus formed is adhesive on the anode surface and it can be easily peeled off after building up sufficient thickness (1 micron). This polymer is quite stable upto \( 150^\circ\)C.

Accordingly, the present invention consists an improved process for the preparation of polypyrrole which comprises electrochemical polymerisation of pyrrole in an electrolyte containing a supporting electrolyte in a solvent the anode and the cathode being stainless steel and having an area 30cm\(^2\).

The invention is further illustrated by the following examples which should not be considered as limiting the scope of the invention.
### Example 1

Supporting electrolyte: Anhydrous sodium perchlorate (1M) in 100 ml of acetonitrile. (Double distilled). The electrolyte was deaerated by passing nitrogen.

<table>
<thead>
<tr>
<th>Pyrrole</th>
<th>0.1M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode area</td>
<td>Stainless steel of 30 cm² area</td>
</tr>
<tr>
<td>Cathode area</td>
<td>Stainless steel of 30 cm² area</td>
</tr>
<tr>
<td>Temperature</td>
<td>Room Temperature (30-35°C)</td>
</tr>
<tr>
<td>C.d. employed</td>
<td>0.006A/cm²</td>
</tr>
<tr>
<td>Cell voltage</td>
<td>2.4V</td>
</tr>
<tr>
<td>Duration of electrolysis</td>
<td>30 minutes</td>
</tr>
<tr>
<td>Thickness obtained</td>
<td>0.1 mm</td>
</tr>
<tr>
<td>C.E.</td>
<td>55%</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1.5 ohm -1 cm -1</td>
</tr>
</tbody>
</table>

### Example 2

Supporting electrolyte: Anhydrous lithium perchlorate (1M) in 100 ml of acetonitrile (Double distilled). The electrolyte was deaerated by passing nitrogen.

<table>
<thead>
<tr>
<th>Pyrrole</th>
<th>0.1M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode area</td>
<td>Stainless steel of 30 cm² area</td>
</tr>
<tr>
<td>Cathode area</td>
<td>Stainless steel of 30 cm² area</td>
</tr>
<tr>
<td>Temperature</td>
<td>Room Temperature (30-35°C)</td>
</tr>
<tr>
<td>Cell voltage</td>
<td>4.5V</td>
</tr>
<tr>
<td>Current Density</td>
<td>0.006A/cm²</td>
</tr>
<tr>
<td>Duration of electrolysis</td>
<td>30 minutes</td>
</tr>
<tr>
<td>Thickness obtained</td>
<td>0.1 mm</td>
</tr>
<tr>
<td>C.E.</td>
<td>55%</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1.8 ohm -1 cm -1</td>
</tr>
</tbody>
</table>

### Example 3

Supporting electrolyte: Anhydrous sodium perchlorate (1M) in 100 ml dimethyl formamide (Double distilled). The electrolyte was deaerated by passing nitrogen.

<table>
<thead>
<tr>
<th>Pyrrole</th>
<th>0.1 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode area</td>
<td>Stainless steel of 30 cm² area</td>
</tr>
<tr>
<td>Cathode area</td>
<td>Stainless steel of 30 cm² area</td>
</tr>
<tr>
<td>Temperature</td>
<td>Room temperature (30-35°C)</td>
</tr>
<tr>
<td>C.d. employed</td>
<td>0.006A/cm²</td>
</tr>
<tr>
<td>Cell voltage</td>
<td>4.5 V</td>
</tr>
<tr>
<td>Thickness obtained</td>
<td>0.2 mm</td>
</tr>
<tr>
<td>C.E.</td>
<td>55%</td>
</tr>
<tr>
<td>Conductivity</td>
<td>0.8 ohm -1 cm -1</td>
</tr>
</tbody>
</table>
Supporting electrolyte: Anhydrous lithium perchlorate (1M) in 100 ml dimethyl formamide (Double distilled). The electrolyte was deaerated by passing nitrogen.

- Pyrrole: 0.1 M
- Anode area: Stainless steel of 30 cm$^2$ area
- Cathode area: Stainless steel of 30 cm$^2$ area
- Temperature: Room Temperature (30-35°C)
- C.d. employed: 0.006 A/cm$^2$
- Cell voltage: 4.5 V
- Duration of electrolysis: 30 minutes
- Thickness obtained: 0.2 mm
- C.E.: 55%
- Conductivity: 0.8 ohm$^{-1}$ cm$^{-1}$

The main advantages of the invention are:

1) No side products are obtained

2) A polymer of high conductivity is obtained

3) This electrochemical polymerisation leads to a clean and elegant method of polypyrrole preparation
We claim:

1. A process for the preparation of polypyrrole which comprises electrochemical polymerisation of pyrrole in an electrolyte containing a supporting electrolyte in a solvent the anode and the cathode being stainless steel and having an area 30cm².

2. A process as claimed in claim 1 wherein the supporting electrolyte is selected from anhydrous sodium perchlorate or lithium perchlorate.

3. A process as claimed in claim 1 and 2 wherein the solvent used is selected from acetonitrile and dimethyl formamide and tetrahydro furan.

4. A process as claimed in any one of the preceding claims wherein the current density employed ranges from 0.001 A/cm² to 0.012 A/cm².

5. A process as claimed in any one of the preceding claims wherein the voltage ranges from 2.4V to 4.5V.

6. A process as claimed in any one of the preceding claims wherein the electrolysis is conducted for a period of 30 minutes.

7. A process as claimed in claims 6 wherein the temperature of the electrolysis is maintained between 30-35°C.

8. An improved process for the preparation of polypyrrole substantially as hereindescribed with reference to the Examples.

Dated this 11th day of June 1985.

(N.R. SUBBARAM)
JOINT ADVISER (PATENTS)
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
PROCESS FLOW SHEET FOR POLYPYRROLE.

Anhydrous CH₃CN or DMF containing Anhydrous NaClO₄ or LiClO₄

PYRROLE

Electrolytic Cell

Stainless Steel

(-)

Stainless Steel

(+) Poly Pyrrole

APPL. no. 556790/84 16/10/55