

GOVERNMENT OF INDIA, THE PATENT OFFICE
214, ACHARYA JAGADISH BOSE ROAD
CALCUTTA-700017.

Complete Specification No. **16055** dated 12th June, 1985.

Application and Provisional Specification No. 555/D-1/84 dated 9th July, 1984.

Acceptance of the complete specification advertised on **26th September, 1987**

Index at acceptance— 70C_{5&6} [LVIII(5)] & 32E/IX(1)].

International Classification— C07d-27/20.

"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 describes the nature of this invention.

PRICE: TWO RUPEES

161055

This is an invention by Dinesh Chandra Trivedi, Venkatasubramanian 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 ($\approx 10^{-9}$ to 10^{-7} ohm⁻¹ cm⁻¹). Moreover various side products of pyrrole are also formed during the chemical reaction which cannot be avoided.

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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 .1M - 1M or Lithium perchlorate of strength .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 l^{-1} . Even traces of oxygen leads to polymers of low conductance. Other solvents such as CH_2Cl_2 and supporting electrolyte such as $N(Bu)_4BF_4$ can be used. A current of .02 to 0.5 amperes ($cd = 0.001A/cm^2$ to $0.012A/cm^2$) depending on the anode area was passed. For a charge density of $24 mc/cm^2$ 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 0.8V 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

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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 (σ) of polypyrrole was found to be 0.5 to 10 $\text{ohm}^{-1} \text{cm}^{-1}$. 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 upto 150°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.

Pyrrrole : 0.1M

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 : 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

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Supporting electrolyte : Anhydrous lithium 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 cm² area

Cathode area : Stainless steel of 30 cm² area

Temperature : Room Temperature (30-35°C)

Cell voltage : 4.5V

Current Density : 0.006A/cm²

Duration of electrolysis: 30 minutes

Thickness obtained : 0.1 mm

C.E. : 55%

Conductivity : 1.8 ohm⁻¹ 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 : 0.006A/cm²

Cell voltage : 4.5 V

Thickness obtained : 0.2 mm

C.E. : 55%

Conductivity : 0.8 ohm⁻¹ cm⁻¹

Example 4

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

Pyrrrole : 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

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

Pyrrrole : 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 : 5.0 V


Duration of electrolysis: 30 minutes

Thickness 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

161055

THE PATENTS ACT, 1970

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 :—

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This invention is developed by Dinesh Chandra Trivedi, Venkatasubramanian Krishnan, Kodethoor Shrivara Udupa and Kummattithidal 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 30cm².

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 .1M - 1M or lithium perchlorate of strength .1M - 1M 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 % - 1%. Even traces of oxygen leads to polymers of low conductance. Other solvents such as CH_2Cl_2 and supporting electrolyte such as $\text{N}(\text{Bu})_4\text{BF}_4$ can be used. A current of .02 to 0.5 amperes ($\text{cd} = 0.001\text{A}/\text{cm}^2$ to $0.012\text{A}/\text{cm}^2$) was passed. For a charge density of $24\text{ mc}/\text{cm}^2$ 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 0.8V 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 micro meters thickness. The conductivity was measured by Four point probe technique and the conductivity (σ) of polypyrrole was found to be 0.5 to 10^{-1} 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°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 161055

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 cm² area
Cathode area : Stainless steel of 30 cm² area
Temperature : Room Temperature (30-35°C)
C.d. employed : 0.006A/cm²
Cell voltage : 2.4V
Duration of electrolysis: 30 minutes
Thickness obtained : 0.1 mm
C.E. : 55%
Conductivity : 1.5 ohm⁻¹ 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 : 0.1M
Anode area : Stainless steel of 30 cm² area
Cathode area : Stainless steel of 30 cm² area
Temperature : Room Temperature (30-35°C)
Cell voltage : 4.5V
Current Density : 0.006A/cm²
Duration of electrolysis: 30 minutes
Thickness obtained : 0.1 mm
C.E. : 55%
Conductivity : 1.8 ohm⁻¹ 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 : 0.006A/cm²
Cell voltage : 4.5 V
Thickness obtained : 0.2 mm
C.E. : 55%
Conductivity : 0.8 ohm⁻¹ cm⁻¹

Example 4 161055

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

Pyrrrole : 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

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:

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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 30cm^2 .
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 $0.001\text{A}/\text{cm}^2$ to $0.012\text{A}/\text{cm}^2$.
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 5 wherein the temperature of the electrolysis is maintained between $30-35^\circ\text{C}$.
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)
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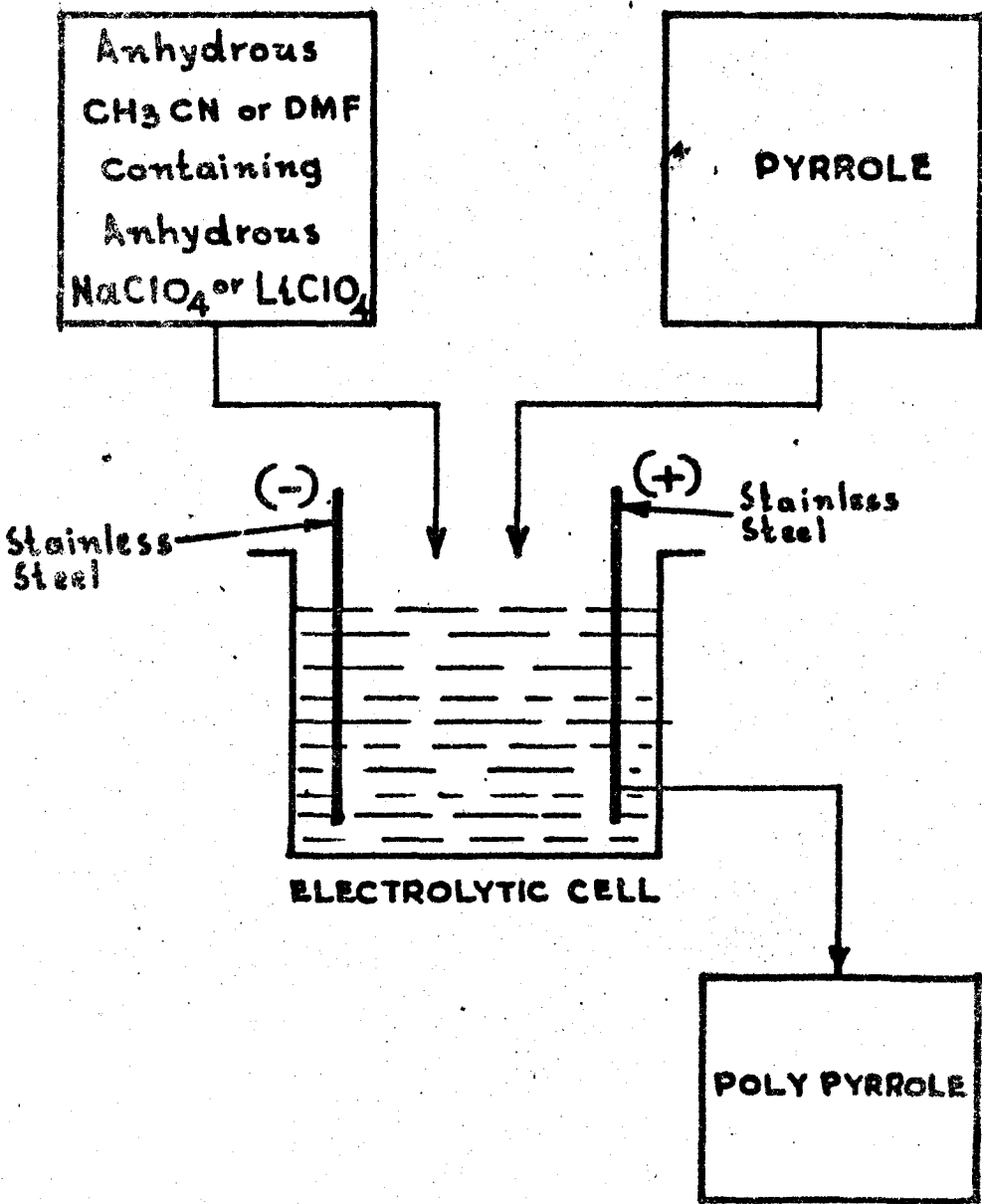
COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC &
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No. OF SHEETS: /
SHEET No.: /

Appn. no. 557/DE/84 161055

PROCESS FLOW SHEET FOR POLYPYRROLE.



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