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" IMPROVEMENTS IN OR RELATING TO ELECTROCHEMICAL SYNTHESIS OF POLYINDOLE".

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

This is an invention by Dinesh Chandra Trivedi, Venkata Subramanian Krishnan, Kodethoor Shrivara Udupa and Kummattithidal Santhanan Rajagopalan scientists of Central Electrochemical Research Institute, Karaikudi, all Indian citizens.

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

This conducting polymer of Indole can be used as material for organic batteries and for the storage of IC chips. The polymerisation could be carried out either in an undivided cell or in a divided cell without affecting the efficiency of polymerisation.

Hitherto the electrochemical polymersation of Indole and the subsequent preparation of poly indole was done on the anodes such as Platinum, Au, SnO_2 and In_2O_3 in an Argon atmosphere.

The Chemical method of polymerisation of Indole leads to the formation of polymer of very low conductivity (10^{-11} to 10^{-8} ohm cm^1). Moreover various oxygenated side products of Indole are also formed during the chemical reaction which cannot avoided.

Hence the main object of this invention is to develop an electrochemical method for the preparation of poly indole,

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 a platinum anode or nickel anode or a stainless steel anode 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 tetrahydrofurn (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 of 24 mc/cm^2 the thickness of 1 mm is obtained. 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 0.9V vs SCE and this is maintained.

The oxidation potential of monomer Indole remains unchanged with different solvents and supporting electrolytes indicating an uniform polymer formation on the anode surface. At an anode potential of 0.9V vs SCE the current increases sharply and gets stabilised after a few minutes. On passing the current the anode surface becomes black due to poly indole 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 of poly indole (0) was found to be 10^{-5} to 10^{-2} ohm^{-1} cm^{-1}. The conducting polymer thus formed is adhesive on the anode surface and it can be easily peeled off after building up of sufficient thickness (0.1mm). This polymer is quite stable.

Following are the examples:

Example-1

Supporting electrolyte	:	Anhydrous sodium perchlorate (1M) in 100 ml of acetonitrile (Double distilled). The electrolyte was deaerated by passing nitrogen
Indole	:	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	:	2.4 V
Duration of electrolysis	:	30 minutes
Thickness obtained	:	0.5 mm
C.E.	:	60%
Conductivity	:	10^{-3} ohm^{-1} cm^{-1}

Example-2

Supporting electrolyte	:	Anhydrous lithium perchlorate (1M) in100 ml of acettonitrile (Double distilled). The electrolyte was deaerated by passing nitrogen
Indole	:	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	:	4.5 V
Duration of electrolysis	:	30 minutes
Thickness obtained	:	0.5 mm
C.E.	:	62%
Conductivity	:	10^{-2} ohm^{-1} cm^{-1}

Example-3

Supporting electrolyte	:	Anhydrous sodium perchlorate (1M) in 100 ml dimethyl form-amide (Double distilled). The electrolyte was deaerated by passing nitrogen
Indole	:	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	:	4.5 V

Thickness obtained	:	0.5 mm
C.E.	:	55%
Conductivity	:	10^{-4} ohm^{-1} cm^{-1}

Dated this 13th January 1984.

(S. CHAKRAVARTY)
PATENTS OFFICER
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

161412

THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section—10)

" IMPROVEMENTS IN OR RELATING TO ELECTROCHEMICAL SYNTHESIS OF POLYINDOLE".

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-110001, India, an Indian registered body incorporate 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, Kodithoor Shrivara Udupa, and Kummattithidal Santhanam Rajagopalan, all of CECRI, Karaikudi Tamil Nadu, India, all Indian citizens and relates to polyindole can been 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 polymerization of indole and subsequent preparation of polyindole was done on the anodes such as Platinum, Au, SnO_2 and In_2O_3 in an argon atmosphere.

The chemical method of polymerization of indole leads to the formation of polymer of very low conductivity (10^{-11} to 10^{-8} ohm^{-1} cm^{-1}). Moreover, various oxygenated side products of indole are also formed during the chemical reaction which cannot be avoided.

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

Accordingly, the invention relates to the electrochemical preparation of poly indole from indole in an electrolyte containing a supporting electrolyte in a solvent 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 and tetrahydro furan.

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

In a 200 ml glass beaker a stainless steel cathode and a stainless steel anode 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). The experiments 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 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) For a chargeof 24 mc/cm^2 the thickness of 1um is obtained. 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 0.9V vs SCE and this is maintained.

The oxidation potential of monomer indole remains unchanged with different solvents and supporting electrolytes indicating an uniform polymer formation on the anode surface. At an anode potential of 0.9V vs SCE the current increases sharply and gets

stabilised after a few minutes. On passing the current the anode surface becomes black due to poly indole formation. The conductance of polymer allows the fast growth of a film of many micro film of many micro meters thickness. The conductivity was measured by four point probe technique and the conductivity of poly indole was found to be 10^{-5} to 10^{-2} cohm $^{-1}$ cm^{-1}. The conducting polymer thus formed is adhesive on the anode surface and it can be easily peeled off after building up of sufficient thickness (0.1mm). This polymer is quite stable.

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.
Indole	:	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	:	0.5 mm
C.E.	:	60%
Conductivity	:	10^{-3} ohm^{-1} cm^{-1}

Example-2

Supporting electrolyte	:	Anhydrous sodium perchlorate (1M) in 100 ml of acetonitrile (Double distilled). The electrolyte was deaerated by passing nitrogen.
Indole	:	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	:	0.006 A/cm^2
Cell voltage	:	4.5V
Duration of electrolysis	:	30 minutes
Thickness obtained	:	0.5 mm
C.E.	:	62%
Conductivity	:	10^{-2} ohm^{-1} cm^{-1}

Example-3

Supporting electrolyte	:	Anhydrous sodium perchlorate (1M) in 100 ml of acetonitrile (Double distilled). The electrolyte was deaerated by passing nitrogen.
Indole	:	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	:	0.006 A/cm^2
Cell voltage	:	4.5 V
Thickness obtained	:	0.5 mm
C.E.	:	55%
Conductivity	:	10^{-4} ohm^{-1} cm^{-1}

The main advantages of the invention are:

(i) No side products are obtained

(ii) A polymer of good and uniform conductivity is obtained

(iii) This electrochemical polymerization leads to a clean and an elegant method of polyindole preparation

We claim:

161412

1. An improved process for the preparation of polyindole which comprises electrochemical polymerization of indole in an electrolyte bath containing a supporting electrolyte in a solvent the anode and the cathode being stainless steel and having an area of 30cm^2C.

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

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

4. A process as claimed in any one of the preceeding claims wherin the current density used ranges from 0.001A cm^2 to 0.012A/cm^2.

5. A process as claimed in any of the preceeding claim wherein the ~~the~~ cell voltage ranges from 2.4 V to 4.5 V.

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

7. A process as claimed in claims 1 to 6 wherein the temperature of electrolysis is maintained between 30-35°C.

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

Dated this 11th day of June 1985.

N R Subbaram

(N.R. SUBBARAM)
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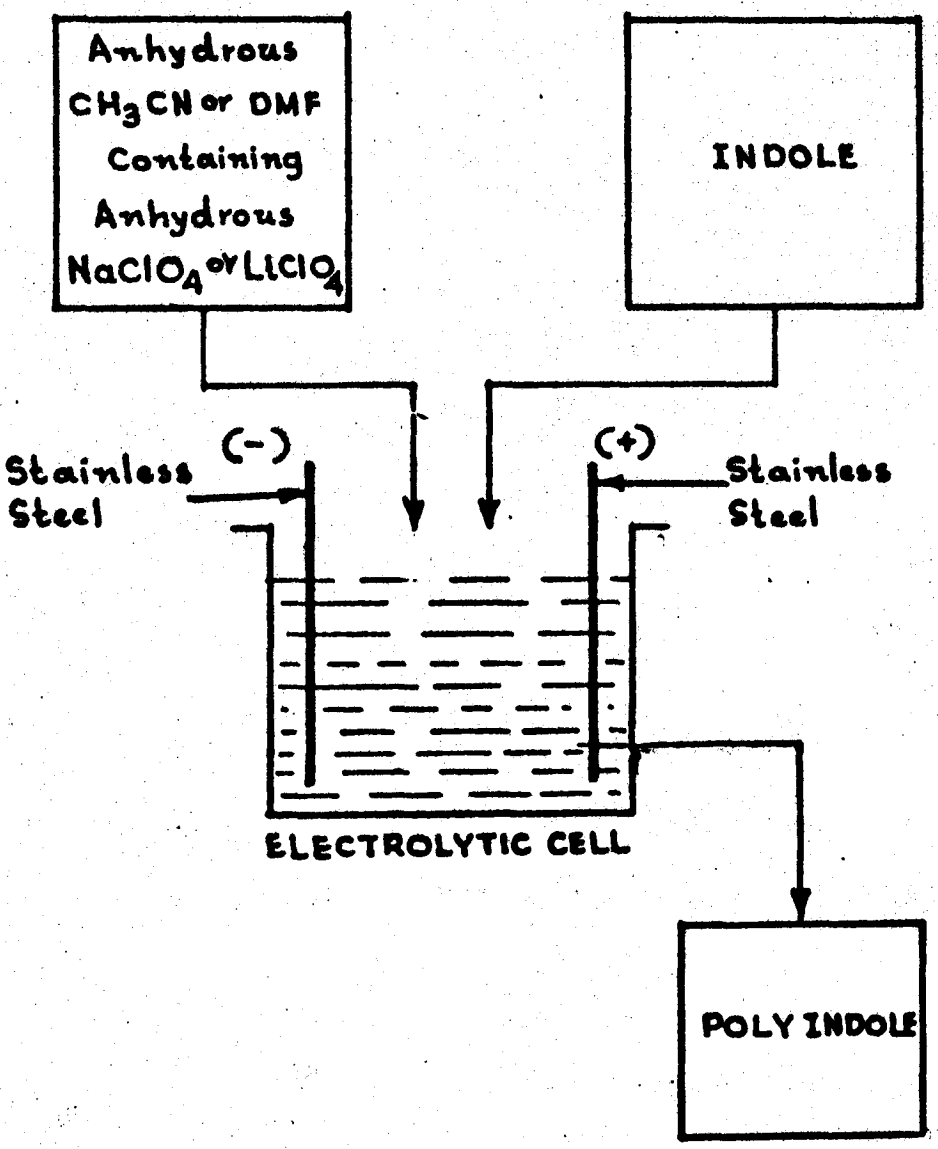
COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

No. OF SHEETS: 1
SHEET No. : 1

APLN. NO. 161/12

PROCESS FLOWSHEET FOR POLY INDOLE.



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