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Title : A PROCESS FOR THE ELECTROSYNTHESIS OF CONDUCTING POLYTHIENE LINES.

Applicant : 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 1960)

Inventor(s) : MUTTANA THEMMANAYAN, SETHURAMAN PITCHUMANI & VENKATA SUBRAMANIAN
KRISHNAN.

The following specification particularly describes and ascertains the
nature of this invention and the manner in which it is to be performed :-

PRICE : TWO RUPEES

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This is an invention by Muthana Thevar Vijayan, Sethuraman Pitchumani, and Venkatasubramanian Krishnan, all of Central Electrochemical Research Institute, Karaikudi-623006 (TN), India and all Indian citizens and relates to the electro^{a process for}synthesis of Polythienylene.

More particularly this invention relates to electropolymerizing thienylene monomer using tetrabutyl ammonium tetrafluoro borate or sodium perchlorate or potassium hexafluoro arsenate as electrolyte on the stainless steel anode. The medium employed may be acetonitrile.

The main objective of this invention is to develop an electrochemical route for synthesising not only p-type, but also n-type and neutral material, by taking into account of the electrochemical reversibility of the system. The major advantage is the product isolation which is simple as it is obtained on electrode surface in the desired form. Further electrochemical route is standardised in such a way that one can obtain the conducting polythienylene at desired conductivity. Thus the overall control of the electrochemical route is achieved to derive the desired level of conducting on the polymer.

Electropolymerization is carried out in a single compartment standard electrochemical cell. The electrolyte medium may be composed of thienylene monomer and an electrolyte in purified acetonitrile. The electrolytes can be either tetra butyl ammonium tetrafluoro borate or sodium perchlorate or potassium hexafluoro arsenate. The entire system is maintained under inert

atmosphere. A current density in the order of $3.5 - 5\text{mA/cm}^2$ can be imposed on the system through a normal circuit depending on the area of anode. The polymer formation is observed as a film or thick deposit on the anode. The polymer thus obtained is insoluble in all common organic solvents. The conductivity of the polymer is measured using a standard method and found in the range $25-100\ \text{Ohm}^{-1}\text{cm}^{-1}$. The time of polymerization can be in the range of 10-20 minutes.

Synthesis of neutral Polythienylene:

In the same set up as described above, neutral Polythienylene can be obtained by undoping the polymer. After changing the polarity of electrode, a current density in the region of $4 - 5\ \text{mA/cm}^2$ is imposed on the system. The neutral film thus obtained on the cathode can be peeled off easily and the conductivity is found to be in the order of $1 - 2 \times 10^{-8}\ \text{Ohm}^{-1}\text{cm}^{-1}$. The electrolytes employed are the same as described earlier. The time of dedoping can be of the order of 30 minutes.

Synthesis of n-type Polythienylene:

This can be synthesised by electrochemical doping on the neutral Polythienylene which is employed as cathode. A current density in the region of $3.5\text{mA} - 5\text{mA}$ can be employed. The electrolytes and their concentration are the same as described earlier. The conductivity of n-type thus obtained is found to be in the order of $0.1 - 0.2\ \text{Ohm}^{-1}\text{cm}^{-1}$. The times of doping process can be in the range of 10 - 25 minutes.

The method leads to Polymer doped with different anions such as BF_4^- AsF_6^- ClO_4^- which imparts characteristic conductivity. The

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process can be achieved using a single compartment electrochemical cell.

The polymer obtained can be used as electroactive material in the fabrication of light weight recharggeable secondary battery. Besides, it can be employed as electrochromic material or as newer electrode.

Following are the advantages:

- i) polythienylene exhibiting n-type, p-type conductivity can be synthesised in a single stroke.
- ii) Cheaper anodes can be employed
- iii) The product is obtained in the desired shape.
- iv) Electrochemical compensation of n and p type conductivity is achieved.
- v) Lesser time is required for all the reactions.
- vi) Thickness, conductivity and composition are precisely controlled by the electrochemical parameters.

Dated this 24th day of March 1986



(N.R. SUBBARAM)
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THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section-10)

Title : A PROCESS FOR THE ELECTROSYNTHESIS OF CONDUCTING
POLYMER(VIOLIN).

Applicant : 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 1950)

Inventor(s) : MUTHANA THEVANAYAN & SETHURAMAN PITCHUMANI & VENKATA--
SUBRAMANIAN KRISHNAN.

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 Muthanna Thevar Vijayan, Sethuraman Pitchumani, Venkatasubramanian Krishnan all of Central Electro Chemical Research Institute, Karaikudi, Tamilnadu, India all Indian citizens and relates to a process for the electrosynthesis of conducting polythienylenes.

The conducting polythienylene prepared can be used as electroactive material in electrochemical devices. No method has so far been known for the preparation of such polymer film.

The process of this invention can be used for the synthesis of p-type, n-type and neutral polythienylene.

Accordingly, the present invention provides a process for the electrosynthesis of conducting polythienylenes which comprises electropolymerising thienylene monomer in a supporting electrolyte selected from acetonitrile containing tetra butyl ammonium tetra fluoroborate, sodium perchlorate or potassium hexafluoro arsenate, in an electro chemical cell having a stainless steel anode and a cathode such as hereindescribed at a current density of 3.5-5A/cm².

The supporting electrolyte may be acetonitrile containing tetrabutyl ammonium, tetra fluoroborate, sodium perchlorate or potassium hexa fluoro arsenate.

This invention broadly consists of the following details :-

Synthesis of p-type polythienylene: Electropolymerization may be carried out in a single compartment standard electrochemical cell. The electrolyte medium is composed of thienylene monomer and an electrolyte in purified acetonitrile. The electrolytes can be either tetra butyl ammonium tetra fluoro borate preferably 0.1M - 0.45M, or sodium perchlorate perferably 0.1M - 0.35M, or

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potassium hexafluoro arsenate preferably 0.05M - 0.25M. The entire system is maintained under nitrogen atmosphere. A current density in the order of 3.5 - 5mA/cm² can be imposed on the system through a normal circuit depending on the area of anode. The polymer formation is observed as a film or thick deposit on the anode. The polymer thus obtained is insoluble in all common organic solvents. The conductivity of the polymer is measured using a standard method and found in the range 25-100 Ohm⁻¹cm⁻¹. The time of polymerization can be in the range of 10-20 minutes.

Synthesis of neutral polythienylene : In the same set up as described above, neutral polythienylene can be obtained by undoping the polymer. After changing the polarity of electrode, a current density in the region of 4-5 mA/cm² is imposed on the system. The neutral film thus obtained on the cathode can be peeled off easily and the conductivity is found to be in the order of 1-2 x 10⁻⁸Ohm⁻¹cm⁻¹. The electrolytes employed are the same as described earlier. The time of dedoping can be of the order of 30 minutes.

Synthesis of n-type polythienylene : This can be synthesised by electrochemical doping on the neutral polythienylene which is employed as cathode. A current density in the region of 3.5 mA - 5mA can be employed. The electrolytes and their concentration are the same as described earlier. The conductivity of n-type thus obtained is found to be in the order of 0.1 -0.2 Ohm⁻¹cm⁻¹. The time of doping process can be in the range of 10-25 minutes.

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The invention is illustrated by the following examples which should not however be construed to limit the scope of the invention.

Example 1

Synthesis of p-type polythienylene with tetrafluoro borate counter ion.

Anode	:	Stainless steel
Cathode	:	Stainless steel
Cell	:	Undivided
Electrolyte	:	0.4M tetra butyl ammonium tetra fluoro borate in acetonitrile
Concentration of monomer	:	0.2M thienylene
Cell voltage	:	2 V
Area of anode	:	5 cm ²
Thickness of film	:	30
Time of polymerization	:	45 minutes
Conductivity	:	100 Ohm ⁻¹ cm ⁻¹
Composition of Polymer	:	[(C ₄ H ₄ S) BF ₄ 0.28 ⁺] X

Example 2

Synthesis of p-polythienylene with perchlorate counter ion.

Anode	:	Stainless steel
Cathode	:	Stainless steel
Cell	:	Undivided
Electrolyte	:	0.3M of sodium perchlorate in acetonitrile
Concentration of monomer	:	0.2M thienylene
Cell. voltage	:	1.8V

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Area of anode : 5 cm²
Current density : 4mA/cm²
Thickness of film : 30
Time of polymerization : 40 minutes
Conductivity : 60 Ohm⁻¹cm⁻¹
Composition of polymer : [(C₄H₄) S (ClO₄)_{0.24}] X

Example 3

Synthesis of p-polythienylene with hexofluoro arsenate counter ion.

Anode : Stainless steel
Cathode : Stainless steel
Cell : Undivided
Electrolyte : 0.2M potassium hexa fluoro arsenate in acetonitrile
Concentration of monomer : 0.2M thienylene
Area of the anode : 5 cm²
Cell voltage : 2.2 V
Current density : 4 mA/cm²
Thickness of the film : 25
Time of polymerization : 20 minutes
Conductivity : 50 Ohm⁻¹cm⁻¹
Composition of polymer : [(C₄H₄S) AsF₆ (0.22)]X

Example 4

Synthesis of neutral polythienylene

Anode : Stainless steel
Cathode : [(C₄H₄) S (BF₄)_{0.28}]X
Cell : Undivided

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Electrolyte : 0.4M tetrabutyl ammonium tetrafluoro borate in acetonitrile

Effective area of the film on cathode : 5 cm²

Current density : 4 mA/cm²

Thickness of the film : 30

Time of dedoping : 30 minutes

Conductivity : $1.2 \times 10^{-8} \text{ Ohm}^{-1} \text{ cm}^{-1}$

Example 5

Synthesis of neutral polythienylene

Anode : Stainless steel

Cathode : $[(\text{C}_4\text{H}_4) \text{S} (\text{ClO}_4)_{0.24}]_x$

Cell : Undivided

Electrolyte : 0.3M sodium perchlorate

Medium : Acetonitrile

Effective area of the film on cathode : 5 cm²

Current density : 4 mA/cm²

Thickness of film : 30

Time of dedoping : 30 minutes

Conductivity : $2.2 \times 10^{-8} \text{ Ohm}^{-1} \text{ cm}^{-1}$

Example 6

Synthesis of neutral polythienylene

Anode : Stainless steel

Cathode : $[(\text{C}_4\text{H}_4) \text{S} (\text{AsF}_6) (0.22)]_x$

Cell : Undivided

Electrolyte : 0.2M potassium hexafluoro arsenate in acetonitrile

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Effective area of the film : 5 cm²
Current density : 4 mA/cm²
Time of dedoping : 30 minute
Conductivity : 1.8×10^{-8} Ohms⁻¹cm⁻¹

Example 7

Synthesis of n-type polythienylene with (Bu₄N)⁺ counter ion.

Anode : p-polythienylene with BF₄ counter ion film
Cathode : Neutral polythienylene film
Cell : Undivided
Electrolyte : 0.4M tetra butyl ammonium tetra fluoro borate in acetonitrile
Area of the electrode : 5 cm²
Cell voltage : 2 V
Current density : 4 mA/cm²
Time of doping : 15 minutes
Conductivity : 0.1 Ohm⁻¹cm⁻¹
Composition of the polymer : [(C₄H₄) S (Bu₄N)_{0.18}]_x

Example 8

Synthesis of n-type polythienylene with Na⁺ counter ion.

Anode : p-type polythienylene with ClO₄ counter ion film
Cathode : Neutral polythienylene
Cell : Undivided
Electrolyte : 0.3M sodium perchlorate in acetonitrile
Area of the electrode : 5 cm²
Current density : 4.5 mA/cm²

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Time doping : 10 minutes
Conductivity : $0.12 \text{ Ohm}^{-1}\text{cm}^{-1}$
Composition of n-type polythienylene obtained: $[(\text{C}_4\text{H}_4)_\text{S} (\text{Na})_{0.16}]_x$

Example 9

Synthesis of n-type polythienylene with K^+ counter ion.

Anode : p-type polythienylene with AsF_6 counter ion film
Cathode : Neutral polythienylene
Cell : Undivided
Electrolyte : 0.2M potassium hexafluoro arsenate in acetonitrile
Area of the electrode : 5 cm^2
Current density : 4.5 mA/cm^2
Time of doping : 25 minutes
Conductivity : $0.1 \text{ Ohm}^{-1}\text{cm}^{-1}$
Composition of the n-type polythienylene obtained : $[(\text{C}_4\text{H}_4)_\text{S} (\text{K})_{0.17}]_x$

The main advantages of this invention are :

- a) Polythienylene exhibiting n-type, p-type conductivity can be synthesised in a single stroke.
- b) Cheaper anodes can be employed.
- c) Lesser time is required for all the reactions.
- d) Thickness, conductivity and compositions are precisely controlled by the electrochemical parameters.

We claim

1. A process for the electrosynthesis of conducting polythiénylenes which comprises electropolymerising thienylene monomer in a supporting electrolyte selected from acetonitrile containing tetra butyl ammonium tetra fluoroborate, sodium perchlorate or potassium hexafluoro arsenate, in an electrochemical cell having a stainless steel anode and a cathode such as hereindescribed at a current density of 3.5-5A/cm².
2. A process as claimed in claim 1 wherein the concentration of the monomer is 0.2M.
3. A process as claimed in claims 1 & 2 wherein the concentration of tetra butyl ammonium tetrafluoro borate ranges from 0.1M to 0.45M.
4. A process as claimed in claims 1-3 wherein the concentration of sodium perchlorate ranges from 0.1M - 0.35M.
5. A process as claimed in claims 1-4 wherein the concentration of potassium hexafluoro arsenate ranges from 0.1M - 0.25M.
6. A process as claimed in claims 1-5 wherein the electro polymerization is effected under nitrogen atmosphere.
7. A process as claimed in claims 1-6 wherein the reaction is effected for a period ranging from 10-30 minutes.
8. A process as claimed in claims 1-7 wherein the cathode employed is also of stainless steel.

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9. A process as claimed in claims 1-8 wherein the cathode used is $[(C_4H_4)_S (BF_4)_{0.28}]_X$ film.
10. A process as claimed in claims 1-9 wherein the cathode used is $[(C_4H_4)_S (ClO_4)_{0.24}]_X$ film.
11. A process as claimed in claims 1-10 wherein the cathode used is $[(C_4H_4)_S (AsF_6)_{0.22}]_X$ film.
12. A process as claimed in claims 1-11 wherein the cathode is neutral polythienylene film.
13. A process as claimed in claims 1-12 wherein the area of cathode and anode is 5 cm^2 .
14. A process for the electrosynthesis of conducting polythienylene substantially as here in described with reference to the Examples.

Dated this 1st day of June 1987



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