CAS 2011 PROCEEDINGS

VOLUME 1

2011 INTERNATIONAL SEMICONDUCTOR CONFERENCE

October 17-19, Sinaia, ROMANIA

NATIONAL INSTITUTE FOR RESEARCH AND DEVELOPMENT
IN MICROTEHNOLOGIES (IMT-Bucharest)

iMT

under the aegis of
Romanian Academy
Electrochemical Society Inc.

IEEE

ELECTRON DEVICES SOCIETY

co-sponsored by
IEEE-Electron Devices Society
Ministry of Education, Research, Youth and Sport
IEEE-Romania Section
Electron Device Chapter

CAS 2011 PROCEEDINGS

VOLUME 2

2011 INTERNATIONAL SEMICONDUCTOR CONFERENCE

October 17-19, Sinaia, ROMANIA

NATIONAL INSTITUTE FOR RESEARCH AND DEVELOPMENT IN MICROTEHNOLOGIES (IMT-Bucharest)

iMT

under the aegis of
Romanian Academy
Electrochemical Society Inc.

IEEE

ELECTRON DEVICES SOCIETY

co-sponsored by
IEEE-Electron Devices Society
Ministry of Education, Research, Youth and Sport
IEEE-Romania Section
Electron Device Chapter

2011 INTERNATIONAL SEMICONDUCTOR CONFERENCE

34th Edition
October 17-19, Sinaia, Romania

CAS 2011 PROCEEDINGS

VOLUME 1

- *Plenary Session*
- *Nanostructures & Nanotechnology*
- *Microphotonics*
- *Microstructures for Bio & Medical Applications*
- *Microsensors*
- *Microsystem Technology*
- *Microwave and Millimeter Devices, Circuits and Microsystems*

IEEE Catalog Number: CFP11CAS-PRT
ISBN: 978-1-61284-171-7
ISSN: 1545-827X

2011 INTERNATIONAL SEMICONDUCTOR CONFERENCE

34th Edition
October 17-19, Sinaia, Romania

CAS 2011 PROCEEDINGS

VOLUME 2

- *Nanostructures & Advanced Materials*
- *Advanced Materials for Micro and Nano Scale*
- *Power Devices*
- *IC's*
- *Modeling*
- *Devices and IC's*
- *IC & Devices*
- *Student Papers*

IEEE Catalog Number: CFP11CAS-PRT
ISBN: 978-1-61284-171-7
ISSN: 1545-827X

ORGANIZING COMMITTEE

General Chairman:	**Dan Dascalu** - IMT-Bucharest, Romania
Technical Program Chair:	**Adrian Rusu** - "Politehnica" University of Bucharest, Romania
Technical Program Vice Chair:	**Mircea Dragoman** - IMT-Bucharest, Romania
	Gheorghe Brezeanu - "Politehnica" University of Bucharest, Romania
Manager:	**Cristina Buiculescu** - IMT-Bucharest, Romania

INTERNATIONAL ADVISORY COMMITTEE

G.A.J. Amaratunga	- Cambridge Univ., UK
N. Barsan	- Tuebingen Univ, Germany
S. Bellucci	- INFN Lab. Nazionali di Frascati, Roma, Italy
C. Bulucea*	- National Semiconductor, CA, USA
S. Cristoloveanu	- CNRS-INPG-UJF, Grenoble, France
D. Dascalu	- IMT-Bucharest, Romania
H. Hartnagel	- Techn. Univ. Darmstadt, Germany
A.M. Ionescu	- EPF, Lausanne, Switzerland
G. Konstantinidis	- FORTH Heraklion, Greece
R. Marcelli	- CNR-IMM, Rome, Italy
S. Melinte	- Univ. Catholique de Louvain, Belgium
J. Millán	- CNM-CSIC, Barcelona, Spain
K. Mutamba	- Infineon Technologies, Germany
L. Pavesi	- Univ. of Trento, Italy
R. Plana	- LAAS-CNRS, Toulouse, France
A. Tugulea	- "Politehnica" Univ. of Bucharest, Romania
F. Udrea	- Cambridge Univ., UK

TECHNICAL PROGRAM COMMITTEE

G. Brezeanu	- Univ. "Politehnica" of Bucharest, Romania
M. L. Ciurea	- INCD - FM*, Bucharest, Romania
D. Cristea	- IMT-Bucharest, Romania
D. Dascalu	- IMT-Bucharest, Romania
M. Dragoman	- IMT-Bucharest, Romania
A. Müller	- IMT-Bucharest, Romania
R. Müller	- IMT-Bucharest, Romania
D. Neculoiu	- IMT-Bucharest, Romania
A. Rusu	- Univ. "Politehnica" of Bucharest, Romania

*INCD - FM - National Institute for R&D in Material Physics

CONTENTS

PLENARY SESSION

Session **N1: NANOSTRUCTURES & NANOTECHNOLOGY 1**
Oral presentations

Session NA: NANOSTRUCTURES & ADVANCED MATERIALS
Poster presentations

CAS 2011

organized by
NATIONAL INSTITUTE FOR
RESEARCH AND DEVELOPMENT
IN MICROTECHNOLOGIES (IMT-Bucharest)

CAS Office:
IMT-Bucharest
126A(32B), Erou Iancu Nicolae Street, R-077190, Bucharest, Romania
Phone: +4021-2690770; +4021-2690774
Fax: +4021-2690772; +4021-2690776
E-mail:cas@imt.ro
http://www.imt.ro/CAS

IEEE Catalog Number: CFP11CAS-PRT
ISBN: 978-1-61284-171-7
ISSN: 1545-827X

POLYSULFONE-POLYANILINE BLEND COMPOSITE MEMBRANE FOR FUEL CELLS APPLICATIONS

C. Baicea[1], O. Dorca[1], A. Cuciureanu[1], R. Trusca[2], C. Trisca-Rusu[3]

*University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Sciences, Str. Gheorghe Polizu 1-7, Bucharest 011061 Romania

E-mail: cristina_m_baicea@yahoo.com

**Metav R&D, Bucharest, Romania

***National Institute for research and Development in Microtechnologies (IMT-Bucharest) 126A(32B), Erou Iancu Nicolae Street, Bucharest 077190, Romania

Abstract–*This paper presents the synthesis and characterization of a composite polysulfone-polyaniline membrane for electrochemical applications. The polysulfone membrane was obtained by the phase inversion process and polyaniline, obtained from the polymerization of p-phenylenediamine in the presence of hydroquinone, was filtered through this membrane. The material was characterized by thermal analysis, Scanning Electron Microscopy and FT-IR spectroscopy.*

Keywords: *composite membrane, phase inversion process, polysulfone, polyaniline, p-phenylenediamine, hydroquinone*

1. INTRODUCTION

In the past few years, there has been a growing interest for the conducting polymers. They combine the electrical properties similar to those of metals and the characteristics of organic polymers such as light weight, resistance to corrosion, flexibility, lower cost and on the other hand the advantage that they can be tailor-made to the requirements of the application through modifications in the polymer structure [1]. Conducting polymers are remarkable materials with a potent application in a number of growing new technologies, such as energy storage, opto-electronic devices, and for the fabrication of chemical sensors [2]. Among the conducting polymers, polyaniline (PANi) is the most prospective due to its wide range of conductivity from insulating to metallic regime, unique redox tunability associated with the chain nitrogen, good environmental stability, low cost, easy synthesis route, and promising applications in various fields, such as metallic corrosion protection, electromagnetic interference shielding, electrostatic discharge, gas, chemical and pH sensors, actuators, separation membranes etc. [1, 3].

A relatively new approach is to synthesize polyaniline from aromatic diamines, like p-phenylenediamine, due to the fact that the new polymer exhibit better chemical functionality, mechanical and thermal properties than the classically obtained polyaniline [4].

978-1-61284-172-4/11/$26.00 © 2011 IEEE

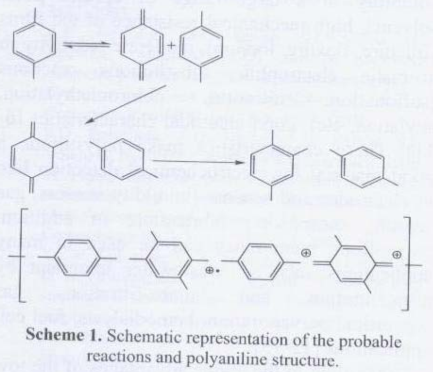
In spite of all these advantages, conducting polymers, including polyaniline, present a poor mechanical strength which limits their applications in some areas including membranes [5]. A solution to this problem is to introduce polyaniline into composite materials. In the present paper polysulfone is used as a blend material for composite membranes due to its remarkable properties.

Polysulfone is widely studied as a polymeric material due to its properties such as: high thermal resistance, chemical resistance on entire pH range, resistance in oxidative medium, solubility in a large range of aprotic polar solvents, high mechanical resistance of the films (fracture, flexure, torsion), moderate reactivity in aromatic electrophile substitutions reactions (sulfonation, nitration, chloromethylation, acylation, etc), good electrical characteristics [6-11]. These characteristics make polysulfone a good material for electrochemical detection like in electrodes and sensors (humidity sensors, gas sensors, biosensors) fabrication, in addition, polysulfone membranes can be used in many applications such as: wastewater treatment by ultra-filtration and micro-filtration, gas separation, pervaporation, hemodialysis, fuel cell applications [12-15].

According to the above advantages of the tow materials, this paper reports the synthesis and characterization of a polysulfone-polyaniline composite membrane obtained by the phase inversion process fallowed by filtration. The new obtained membrane was characterized by thermal analysis, FT-IR spectroscopy and Scanning Electron Microscopy.

2. METHODS

The polysulfone-PSf polymer was supplied by BASF (Ultrason S3010). The polymer was further purified by re-precipitation from chloroform with methanol and dried in vacuum at 60°C. As solvents for polysulfone N, N'-dimethylformamide (DMF), and chloroform (Fluka) were used. As non solvents for membrane phase inversion process, water, methanol and propanol were used. For the synthesis of polyaniline, p-phenyilenediamine, hydroquinone, hydrochloric acid (HCl), potassium persulfate ($K_2S_2O_8$) and water were used. The polysulfone solution was prepared by introducing the required amount of solvent (DMF) into an Erlenmeyer glass and adding small portions of polymer, under magnetic stirring, until the desired concentration was achieved (15%). The air was then removed from solution into a desicator under vacuum for 30 minutes. The polysulfone membrane was formed by depositing a small amount of polymer solution onto a spectral glass with a standard thickness of the membrane fixed at 250μm for. The polymer film deposited on glass was immersed into the coagulation bath which contains 200 mL mixture water : propanol 1: 1.



Scheme 1. Schematic representation of the probable reactions and polyaniline structure.

The polyaniline was obtained by dissolving p-phenylenediamine in a solution of water and HCl, then hydroquinone was added to this solution and in order to induce the polymerization of polyaniline, potassium persulfate was added. The polyaniline presence can be observed due to the fact that a black precipitate is formed.

From the oxidative polymerization of p-phenylenediamine in the presence of small amounts of hydroquinone results a polymer with a doped polyaniline-like structure with semi-quinoid and quinoid rings [4] and probably with hydroquinone bridges intercalated, as it can be seen in scheme 1.

The polyaniline is introduced into the polysulfone membrane by filtering the polymer solution obtained above through the membrane.

3. RESULTS

From the thermal analysis of the obtained composite membrane, presented in figure 1, it can be observed a maximum loss point at 512,8°C specific for polysulfone and a maximum loss point at 555,07°C specific for polyaniline. The shape of the thermo-gravimetric graph indicate that no chemical interaction appear between those two polymers. The advantage of using polysulfone as a matrix for polyaniline is given by the highly thermal and chemical resistance. Conductive polyaniline based devices like sensors and microcapacitors can be manufactured for harsh work conditions (oxidative media, high temperature).

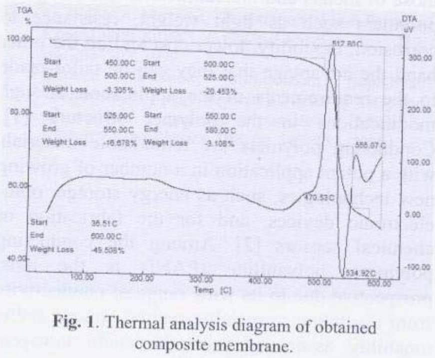


Fig. 1. Thermal analysis diagram of obtained composite membrane.

The SEM analysis images, presented in figure 2, reveal a homogenous material with polyaniline fibres intercalated with polysulfone macromolecular fibres (fig. 2. a, b, c). An interesting morphology presents the membrane in cross-section (fig. 2. d), unusual for a membrane obtained by phase inversion (not very symmetrically).

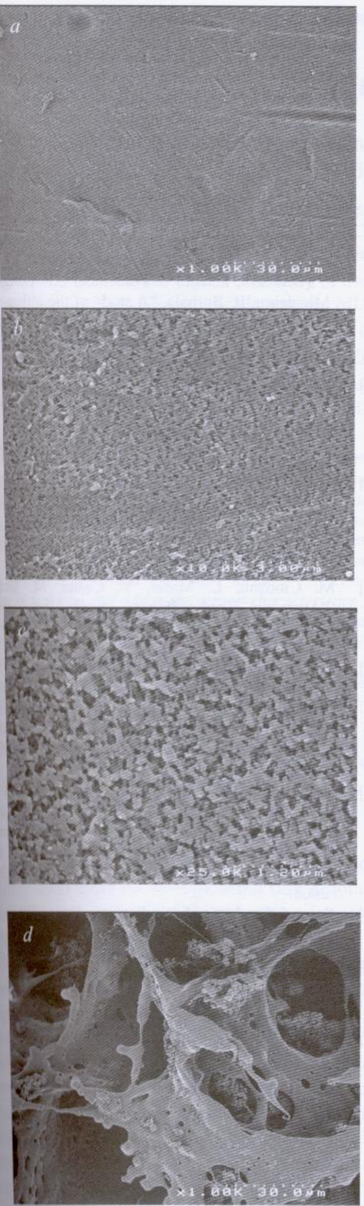


Fig. 2. SEM images of obtained composite membrane, top surface (a-x1000, b-x10000, c-x25000) and cross section (d-x1000).

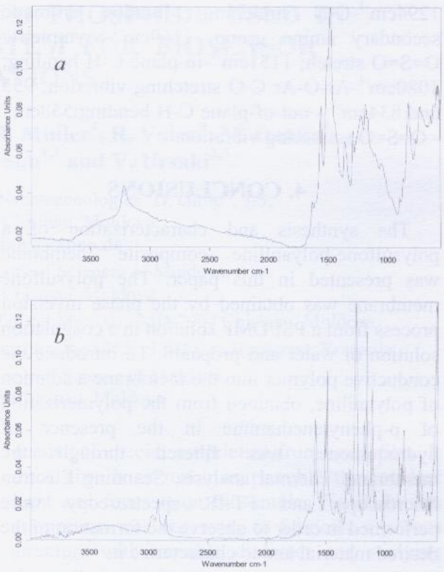


Fig. 3. FT-IR spectrum of polyaniline (a) and polysulfone-polyaniline composite membrane (b).

In the FT-IR spectrum presented in figure 3 the specific peaks and bands for polyaniline and polysulfone-polyaniline membrane can be observed. The assigned vibrational signals for polyaniline obtained by the polymerization of p-phenylenediamine in the presence oh hydroquinone (fig. 3. a) are as fallows: 3215cm^{-1} (3000-3250cm^{-1})-O-H stretching vibration attributed to the O-H group from hydroquinone; 1560cm^{-1}-asymmetric C_6 ring stretching attributed to the quinoid ring; 1487cm^{-1}-asymmetric C_6 ring stretching attributed to the benzoid ring; 1358cm^{-1}-O-H deformation C-O stretching vibration interaction; 1289cm^{-1}-C-N stretching vibration aromatic secondary amino group; 824cm^{-1}-C-H aromatic deformation. The assigned vibrational signals for the composite membrane (fig. 3. b) are as follows: the band from 3000 to 3250cm^{-1}-O-H stretching vibration attributed to the O-H group from hydroquinone; 2969cm^{-1}-C-H asymmetric stretch for CH_3 group; 2850cm^{-1}-C-H symmetric stretch for CH_3 group; 1585cm^{-1}-asymmetric C_6 ring stretching (quinoid ring); 1504cm^{-1}-asymmetric C_6 ring stretching (benzoid ring); 1323cm^{-1}-symmetric O=S=O stretching vibration from sulfone group;

1294cm^{-1}-C-N stretching vibration aromatic secondary amino group; 1169cm^{-1}-asymmetric O=S=O stretch; 1151cm^{-1}-in-plane C-H bending; 1080cm^{-1}-Ar-O-Ar C-O stretching vibration; 955 and 834cm^{-1} - out-of-plane C-H bending;558cm^{-1} - O=S=O scissoring vibration.

4. CONCLUSIONS

The synthesis and characterization of a polysulfone-polyaniline composite membrane was presented in this paper. The polysulfone membrane was obtained by the phase inversion process from a PSf/DMF solution in a coagulation solution of water and propanol. To introduce the conductive polymer into the membrane a solution of polyaniline, obtained from the polymerization of p-phenylenediamine in the presence of hydroquinone, was filtered through the membrane. Thermal analysis, Scanning Electron Microscopy and FT-IR spectroscopy were performed in order to observe the formation of the desired material and to characterize it.

Acknowledgement–The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/88/1.5/S/60203.

References

[1] Srinivasan Palaniappan, Amalraj John, "Polyaniline materials by emulsion polymerization pathway", *Prog. Polym. Sci.*, **33**, pp. 732–758, 2008.

[2] W.P. Jakubik, M. Urbanczyk, E. Maciak, T. Pustelny, A. Stolarczyk, "Polyaniline thin films as a toxic gas sensors in saw system", *Molecular and Quantum Acoustics*, **28**, pp. 125–129, 2007.

[3] Donghua Zhang, Yangyong Wang, "Synthesis and applications of one-dimensional nano-structured polyaniline: An overview", *Materials Science and Engineering B*, **134**, pp. 9–19, 2006.

[4] Ricardo H. Sestrem, Daniela C. Ferreira, Richard Landers, Marcia L.A. Temperini, Gustavo M. do Nascimento, "Structure of chemically prepared poly-(para-phenylenediamine) investigated by spectroscopic techniques", *Polymer*, **50**, pp. 6043–6048, 2009.

[5] A. Bhattacharya, D.C. Mukherjee, J.M. Gohil, Y. Kumar, S. Kundu, "Preparation, characterization and performance of conducting polypyrrole composites based on polysulfone", *Desalination*, **225**, pp. 366–372, 2008.

[6] S.I. Voicu, A.C. Nechifor, B. Seban, G. Nechifor, M. Miculescu, "Formylated polysulfone membranes for cell immobilization" *Journal of Optoelectronics and Advanced Materials* **9**(11), pp. 3423–3426, 2007.

[7] G. Nechifor, S.I. Voicu, A.C. Nechifor, S. Garea, "Nanostructured hybrid membrane polysulfone-carbon nanotubes for hemodialysis", *Desalination*, **241**, pp. 342–348, 2009.

[8] F. Miculescu, I. Jepu, C.P. Lungu, M. Miculescu, M. Bane, "Researches regarding the microanalysis results optimisation on multilayer nanostructures investigations", *Digest Journal of Nanomaterials and Biostructures* **6**(2), pp. 769–778, 2011.

[9] F. Miculescu, I. Jepu, C. Porosnicu, C.P. Lungu, M. Miculescu, B. Burhala, "A study of the influence of the primary electron beam on nanodimensional layers analysis," *Digest Journal of Nanomaterials and Biostructures* **6**(1), pp. 307–317, 2011.

[10] C. Corobea, D. Donescu, S. Răduţoiu, S.I. Voicu, G. Nechifor, "Membrane materials IV. Functionalised hybrid polimer nanoparticles for copper ions separation on colloidal ultrafiltration", *Revista de Chimie*, **57**, pp. 981–987, 2006.

[11] A.C. Nechifor, M.G. Stoian, S.I. Voicu, G. Nechifor, "Modified Fe_3O_4 colloidal dispersed magnetic particles as carrier in liquid membranes," Optoelectronics and Advanced Materials – Rapid Communications **4**(8), p. 1118–1123, 2010.

[12] M. Ciobanu, L. Marin, V. Cozan, M. Bruma, "Aromatic polysulfones used in sensor applications", *Rev. Adv. Mater. Sci.*, **22**, pp. 89–96, 2009.

[13] Shih-Hsiung Chen, Rey-May Liou , Juin-Yih Lai, Cheng-Lee Lai, "Efect of the polarity of additional solvent on membrane formation in polysulfone/N-methyl-2-pyrrolidone/water ternary system", *European Polymer Journal*, **43**, pp. 3997–4007, 2007.

[14] Jianyu Wang, Youyi Xu, Liping Zhu, Jianhua Li, Baoku Zhu, "Amphiphilic ABA copolymers used for surface modification of polysulfone membranes, Part 1: Molecular design, synthesis, and characterization", *Polymer*, **49**, pp. 3256–3264, 2008.

[15] Samuel Sánchez , Martin Pumera , Esteve Fábregas, "Carbon nanotube/polysulfone screen-printed electrochemical immunosensor", *Biosensors and Bioelectronics*, **23**, pp. 332–340, 2007.