Macromol. Symp. ***188,*** *1–12 (2002)*

Conductive Polymer Membranes

J. SARRAZIN, M. PERSIN, M. CRETIN*

Institut Européen des Membranes, UMR 5635 CNRS, ENSCM, UM2, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France
E-mail: sarrazin@cit.enscm.fr

Summary: A survey of the literature devoted to membranes based on polypyrroles issued from pyrrole or from its derivatives shows that their properties depend on their doped/undoped state and that they can be employed in sensors or separation devices. Some results are given in ion exchange properties and ETBE/ethanol separation by pervaporation.

Introduction

Conductive polymers, often qualified of synthetic metals, are materials combining properties of organic polymers and electric conduction (semiconductors). They have been intensively studied during the last decades. Actually, though the first aniline and pyrrole blacks were produced as early as respectively 1862 [1] and 1916 [2], systematic studies in that field appeared only in the last quarter of the 20th century. The first works were devoted to donor-acceptor complexes [3-5] and then to polyacetylene when it was shown that doping by iodine could lead to an electronic conductivity of 10^3 $S.cm^{-1}$ [6]. Since Diaz et al [7] synthesised electrochemically the first flexible, stable polypyrrole (PPy) film of high conductivity (100 $S{\cdot}cm^{-1}$), a tremendous amount of researches has been focused on conducting polymers. It opened the way to the preparation of numerous other conductive polymers. So, in 1982 Tourillon and Garnier prepared polythiophene, polyfuranne, polyindole and polyazulene [8]. Today, dozens of conductive polymers have been obtained which were reviewed in a recent book [9]: polyacetylene [10], polythiophenes [11-13], polypyrroles [14], polyaniline [15]. The main characteristic of these polymers is their conjugated π system, which extends beyond the monomer and allows an electron delocalisation along the polymer chain and gives a conductive character to the material.

Two ways of synthesis can be operated for the preparation of conductive polymers: chemical and electrochemical.

CCC 1022-1360/00/$ 17.50+.50/0

Chemical Synthesis

The chemical synthesis can be performed by varied methods: by oxidation or reduction of monomer, in liquid or gas phase, sometimes by thermal autopolymerisation. The resulting products are often oligomers or polymers presenting a low specific conductivity. So the first chemical polymerisation of pyrrole was performed by oxidation of pyrrole by means of hydrogen peroxide and afforded a black powder insoluble in organic solvents [2 , 16]. Preparation with acetic acid or hydrogen peroxide leads to a material of weak specific conductivity (10^{-10} - 10^{-11} cm^{-1}) [17-19]. By doping with an halide, the specific conductivity was increased to 10^{5} cm^{-1} [20]. Other examples of oxidising agents were reported (2,3 dichloro 5,6 dicyano-parabenzoquinone (DDQ), chloranile,...) in preparations leading to polypyrroles of specific conductivities between 10^{-5} and 10^{-1} cm^{-1} [21]. Others oxidising agents can be used: acetic acid, iron III chloride, nitric acid, quinones, ozone... In most cases, salts of oxidising metals are employed.

Electrochemical Synthesis

The electrochemical synthesis is performed in solution, aqueous or not, in the presence of an electrolyte. Conductive polymers can be prepared by cathodic reduction of some substrates but anodic oxidation of monomer is the technique generally employed for the electrosynthesis of conductive polymers. Polymers obtained by this way are in an oxidised state because the oxidation potential of the monomer is generally higher than that of the formed polymer. The polymers are doped because the electroneutrality of the material is assured by the presence of counter-ions (anions) compensating for the positive charge carried by the skeleton in the oxidised state. On the other hand, the layer deposited on the surface of the electrode being conductive, the deposit can occur at the surface of the polymer. The electrochemical conditions allow a precise control of the deposit.

This paper is mainly focused on polypyrrole derivatives. A survey of the literature in the field of membranes based on polypyrroles issued from pyrrole or from its derivatives allows to identify three types of concerns in the reported works:

- the preparation of polypyrroles films and the study of the physico-chemical properties of the resulting material.
- the implication of these films in sensors.
- the transport through membranes, either composite (often porous) or dense polypyrrole membranes.

Preparation and Physico-chemical Properties of Polypyrrole Films

The polypyrrole is generally obtained by anodic oxidation of a solution of the monomer containing a supporting-electrolyte. The oxidation potential of the polymer being lower than that of monomer, the polymer is obtained in the oxidised state and it is doped by the anion of the supporting-electrolyte. The general equation of the electropolymerisation reaction of can be written as follows.

$$x\,(Py) - (2x + y)\,e^- - 2x\,H^+ + yA^- \rightarrow (Py)_x^{y+}, y\,A^- \quad (1)$$

where A^- is the counter-ion , x the degree of polymerisation of the heterocycle, y the oxidation degree of the polymer.

In our laboratory, an insertion degree $y/x = 0{,}2$ was reached for PF_6^- in polypyrrole [22]. The nature of the anion, by its size, its charge and its geometry, plays a fundamental role towards the mechanical, electric and chemical properties of the polymer, and consequently towards the behaviour of the membrane. A big variety of anions could be incorporated into polypyrrole films. For example, the specific conductivity of the polypyrrole passes from 10^{-2} to 10^{2} cm^{-1} when a sulfonate anion is used instead of a perchlorate [23]. Other authors showed that they obtain a doping rate of 25 % while it is 50 % with NO_3^- in aqueous medium [24]. Besides, the stability of the anion insertion depends on the nature of this anion. Generally speaking, such an anion may be eliminated from the material either by ion exchange, when the material is put in contact with of an ionic solution, or by reduction of the polymer, which can occur with the ejection of the counter-anion. However, if the affinity of the anion incorporated in the material is high enough, the reduction of the polymer leads to the trapping of a cation instead of the eviction of the anion. So, according to the conditions of their preparation and their use, polypyrroles can behave as anion or cation exchangers.

The use of a quartz crystal microbalance (QCM) allows to obtain semi quantitative data during the electropolymerisation and on the doping and undoping processes because this technique allows to measure very weak mass variations. Figure 1 and figure 2 show examples of the influence of the medium on the behaviour of the film. In acetonitrile with tetrabutylammonium hexafluorophosphate, the anion is incorporated into the polypyrrole film at the oxidation step and rejected at the reduction step (fig. 1c, d). In the case of water acetonitrile (70/30) mixture with sodium paratoluenesulfonate, sodium ejection and anion insertion are successively observed during the anodic scan, and the electroreduction during the reverse scan, leads to successive anion ejection and cation insertion (fig. 2c, d).

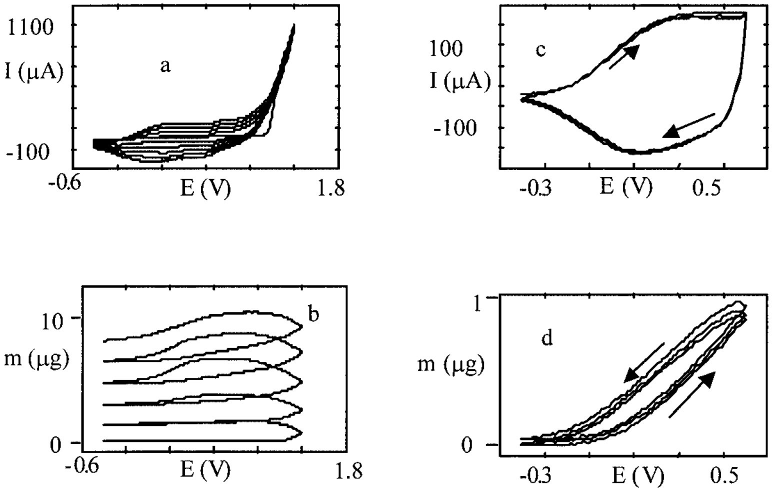

Figure 1. Cyclic voltammetry (0.1 V/s) (a, c) and QCM measurements (b, d) in CH_3CN, 0.1 M NBu_4PF_6. Electropolymerisation of pyrrole (5 10^{-3} M) (a, b). polypyrrole film in the absence of monomer (c, d).

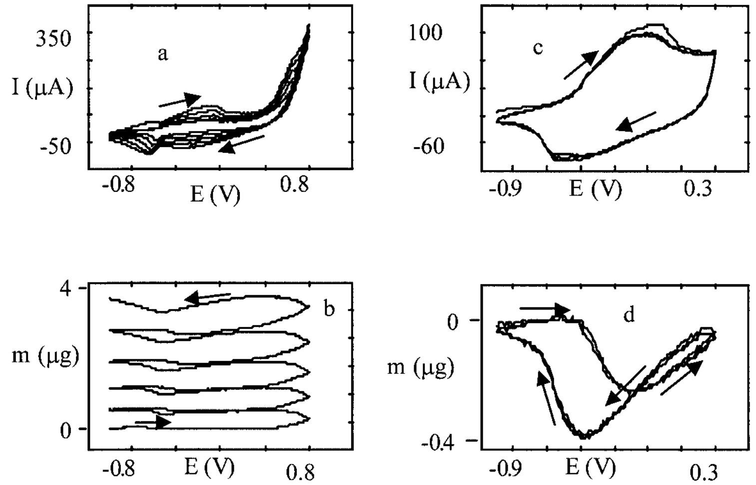

Figure 2. Cyclic voltammetry (0.1 V/s) (a, c) and QCM measurements (b, d) in H_2O/CH_3CN (7/3), 0.1 M sodium paratoluenesulfonate. Electropolymerisation of pyrrole (5 10^{-3} M) (a, b). polypyrrole film in the absence of monomer (c, d).

Polypyrrole can be switched from cation exchanger to anion exchanger by variation of the potential applied to the film or by variation of the pH of the solution. So heparin is trapped in a permanent way in polypyrrole and the material behaves as a cation exchanger. However, in acidic environment, it works as an anion exchanger [25]. Trapping of organic anions with a long chain leads to a character of anion exchanger in the oxidised state and of cation exchanger in the reduced state [26, 27]. The insertion of inorganic anions such as polyoxoanions [28] or hexacyanoferrates [29] was also studied. The insertion of naphtalenesulfonates [30], the behaviour of polypyrroles films dipped into a solution of tosylate [31], and the preparation of films from tosylate solutions [32] was followed by QCM measurements.

Polypyrrole was used as an electrochemical pump for cations: heavy metals are transferred from a solution to the polypyrrole by electroreduction of the material ; they can then be released into another solution by oxidation [33]. Other studies concerned the permeability of the membrane towards anions and/or towards cations according to the oxidation state of the membrane material [34-36].

Electrochemical impedance spectrometry also gives indications about the doping state and the ion conduction of the material [37-39]. The rate of charged species transport in polypyrrole was studied [40] and anion conductivity and permselectivity to anions in the oxidised state were shown by measures in alternating and direct currents [41].

Sensors

The use of polypyrrole films in sensors is based on the conductive properties of the material, on its properties of ion exchanger or on the possibilities of immobilising enzymes in the material during the synthesis.

A potentiometric sensor of humidity was proposed, constituted of an anion exchange membrane coated with a polypyrrole layer on each side [42]. The voltage between both faces depends on the humidity and the sensitivity of the system depends on the nature of the incorporated anion.

A potentiometric answer to the presence of ions in solution was shown with electrodeposited polypyrrole films. These systems can answer the cations or the anions according to the charge of counter-ions incorporated during the synthesis [43]. An anion answer was observed with films doped by small inorganic ions as chloride, nitrate or perchlorate [44-47]. The weak selectivity of such systems was analysed [48]. A potentiometric answer to the presence of cations in solution could be obtained by means of polypyrrole films in which of voluminous anions were inserted [49-51]. A selectivity could be observed when this incorporated anion presents properties of complexation of the species to be analysed. So, the incorporation of "calcion " allows the detection of the Ca^{2+} ion [52]. The conditions of preparation of the polymer also influence the properties of the sensor [43, 53].

All solid sensors, the advantage of which being that they can easily be miniaturised, were finalised for the detection of sodium and potassium in solution. For the detection of sodium [54], the device contains a platinum electrode, coated with an intermediate layer of polypyrrole electrochemically doped by BF_4^- and then a PVC layer incorporating a calixarene selective of sodium. A practically identical system, using a crown-ether adapted to sodium was studied [55]. Other authors use an intermediate composite layer constituted by polypyrrole and polystyrene-sulfonate and use of vanilomycin in a PVC layer to obtain the desired selectivity for potassium [56-58]. The use of similar systems was proposed for the potentiometric detection of anions in capillary electrophoresis [59].

It was also shown that square wave voltammetry with a polypyrrole modified electrode containing disulfonates of bathophenanthrolin and bathocuproïn, anionic ligands, allowed the analysis of copper in solution [60].

Enzyme Sensors

In a general way, "enzyme electrodes" are electrochemical devices which give an electric signal in answer to the presence of a species, the selectivity being due to the presence of an enzyme immobilised in a membrane. The species to be analysed gives a reaction catalysed by the enzyme and the electrochemical device allows to follow, generally in a potentiometric or amperometric way, the consumption of one of the reagents involved or the production of one of the products of the enzymatic reaction.

Enzymes could be incorporated into polypyrrole films and the properties of the sensors based on these systems were studied. So, for example, the immobilisation of glucose oxidase in polypyrrole allows an amperometric detection of glucose in solution [61]. Other authors showed that the simultaneous immobilisation of a coenzyme (flavin) increases the current density [62]. Also let us note that glucose oxidase maybe activated or deactivated by simple modification of the potential applied to the polypyrrole [63]. Several other substrate / immobilised enzyme pairs involving polypyrrole can be found in the literature of these last years: lactate / lactate oxidase [64], urea / urease [65], hydrogen peroxide / peroxidase [66-68], fructose / fructose [69]. Let us also note some attempts to exploit the properties of polypyrrole in the form of tubules deposited by chemical way in the pores of porous membranes [70, 71]. Polypyrrole was also proposed to improve the electrode / BLM interface in electrochemical sensors with enzymes immobilised on BLM [72]. Indeed, the authors showed that the BLM deposited on polypyrrole is more homogeneous than that deposited on the metal.

Conduction

The change of the material resistivity when it is immersed in a solution can be exploited to obtain information on the considered medium. A pH sensor based on polypyrrole and working on this principle was proposed recently [73].

The conduction properties of the polypyrrole can be also exploited in the simple use of the polymer as electrode material. Such a device allows for example the amperometric detection of ammoniac [74]. The theoretical study of the penetration of the polypyrrole by the substrate to be oxidised or to be reduced and the modelling of the concentration profiles allow understanding the system behaviour (example of ascorbate) [75].

Let us also note that the use of overoxidised polypyrroles can be a means to improve the selectivity of an amperometric sensor ; this was reported for the detection of formate [76], of dopamine [77] or of hydrogen peroxide. In this latter case, the authors attempted to correlate the permselectivity and the structure of the overoxidised material [78]. Some other few authors considered the control of the permeability of polypyrrole overoxidised films [79].

Separation of Ions in Solution

Besides the films of polypyrrole, the properties of which were presented first, the literature makes appear some attempts of preparation of membranes associating of the polypyrrole to the other materials.

So, the electropolymerisation of pyrrole in contact of a gel of Nafion leads to a material presenting simultaneously ion and electron conductions [80, 81]. Other attempts concerned the realisation of polypyrrole membranes with two layers, each layer being doped by a different anion (paratoluenesulfonate, dodecylsulfate). The result was a membrane presenting a transport asymmetry and selectivity in the transport of sodium towards that of potassium [82].

Other authors investigated the deposition of polypyrrole in the pores of porous membranes made of another material such as PMMA [83], polyethylene [84-86], cellulose [87] or PVDF [88]. This leads to membranes with modified filtration properties, by change of the hydrophilic character of the pores surface, or to dense ion exchange membranes.

Sata, as for him, was interested in the preparation and the properties of membranes associating an ion exchange membrane and a layer of polypyrrole chemically deposited on the surface. This involved anion exchange membranes [89] or of cation exchange membranes [90-92]. The deposition of polypyrrole allows reducing the proton leakage and consequently the permeability of acids through anion exchange membranes [93]. It allows to introduce a selectivity alkaline earth / sodium in the case of electrolytic transport through the cation exchange membrane / polypyrrole composite [94]. A lithium cell based on such a composite has been realised [95].

Composite membranes involving polypyrrole were also tested in the manufacture of all polymer all solid cells [96].

Wallace *et al* investigated the transport of ions and salts through various polypyrrole membranes and studied the parameters influencing this transport [97]. They showed that the transport of salt such as KCl [98] or of ions such as $Cu2^+$ [99] can be regulated by the potential applied to the material. Also, the nature of counter-ion introduced in the synthesis modifies the properties of transport [100]. The use of dodecylsulfate and paratoluenesulfonate leads to an asymmetry in the properties of transfer of the membrane [101]. The thickness of the film is also an important parameter for the permeability to some species such as NADH [102]. Among the species the transport of which was studied by Wallace, [103] let us note aromatic sulfonate anions.

Gas Separation and Pervaporation

Some attempts of application of polypyrroles for gas separation such as oxygen / nitrogen were reported [104]. As for us, we focused on the separation of liquids by pervaporation [22, 105, 106].

For example, due to the growing demand of MTBE and ETBE as good additives for octane improvement of gasoline, and to the interest of the separation of reactant ethanol from product ETBE in the production process, we investigated the separation of ethanol from ETBE by pervaporation through doped polypyrrole membranes. Polymer films incorporating two kinds of doping anions, i.e. hexafluorophosphate (PF_6^-) and tetrafluoroborate (BF_4^-), were electrosynthesised as previously described [105], under controlled potential, on stainless steel meshes in acetonitrile (0.1 M pyrrole, 0.1 M supporting electrolyte and 1 wt.% H_2O). The results [107] obtained are listed in table 1.

Table 1. Pervaporation performance of PF_6^- doped polypyrrole (PPy-PF) and BF_4^- doped polypyrrole (PPy-BF) membranes for ethanol removal from ETBE (t=70°C).

		EtOH in Feed		
		5%	10%	20%
PPy-PF	Flux (g/hm^2)	17	23	34
	EtOH in Perm.	>99%	>99%	>99%
PPy-BF	Flux (g/hm^2)	4	4	6.6
	EtOH in Perm.	95%	98.5%	95%

Both of the membranes display a good selectivity to ethanol but fluxes, which are in the same order of magnitude as the case of ethanol/cyclohexane [26], are too low from the viewpoint of application. Comparatively speaking, the PPy-PF is better than PPy-BF.

References

[1] H. Letheby, *J. Amer. Chem. Soc.* **1862**, 15, 161.

[2] A. Angeli, *Gazz. Chim. Ital.* **1916**, 46, 279.

[3] I. F. Shchegolev, *Phys. Status Solidi A* **1972**, 12, 9.

[4] J. H. Perlstein, *Angew. Chem.* **1977**, 16, 519.

[5] E. P. Goodings, *Chem. Soc. Rev.* **1976**, 5, 95.

[6] C. K. Chiang, C. R. Finger, Y. W. Park, A. J.Heeger, H. Shirakawa, E. J. Lois, S. C. Gao et A. G. Mc Diarmid, *Phys. Rev. Lett.* **1977**, 39, 1098.

[7] A. F. Diaz, K. K. Kanazawa, G. P. Gardini, *J. Chem. Soc. Chem. Commun.* **1979**, 635.

[8] G. Tourillon, F. Garnier, *J. Electroanal. Chem.* **1982**, 135, 173.

[9] H. S. Nalwa (ed.), « Handbook of Organic Conductive Molecules and Polymers », New York, 1997.

[10] S. Curran, A. Stark-Hauser, S. Roth, in « Handbook of Organic Conductive Molecules and Polymers », Vol. 2, H. S. Nalwa (ed.), New York, 1997.

[11] K. Kaeriyama, in « Handbook of Organic Conductive Molecules and Polymers », Vol. 2, H. S. Nalwa (ed.), New York, 1997.

[12] S. Hotta, « Handbook of Organic Conductive Molecules and Polymers », Vol. 2, H. S. Nalwa (ed.), New York, 1997.

[13] J. Roncali, *Chem. Rev.* **1992**, 92, 711.

[14] J. Rodriguez, H. J. Grande, T. F. Otero, « Handbook of Organic Conductive Molecules and Polymers », Vol. 2, H. S. Nalwa (ed.), New York, 1997.

[15] D. C. Trivedi, Handbook of Organic Conductive Molecules and Polymers, Vol. 2, H. S. Nalwa (ed.), New York, 1997.

[16] A. Angeli, L. Alessandri., *Gazz. Chim. Ital.* **1916**, 46, 283.

[17] G. P. Gardini, *Adv. Heterocycl. Chem.* **1973**, 15, 67.

[18] M. Salmon, K. K. Kanazawa, A. F. Diaz, M. T Krounbi, *J. Polym. Lett. Ed.* **1982**, 20, 187.

[19] H. S. Nalwa, L. R. Dalton, W. F. Schmid, J. G. Rabe, *Polym. Commun.* **1985**, 27, 240.

[20] H. Naarmaan, N. Theophilou, *Synth. Met.* **1987**, 22 , 1.

[21] E. T. Kang, G. Neoh, T. C.Tan, Y. K. Ong, *J. Polymer Sci.* **1987**, 25, 2143.

[22] M. Zhou, M. Persin, W. Kujawski, J. Sarrazin, *J. Memb. Sci.* **1995**, 108, 89.

[23] M. Salmon, A. F. Diaz, A. J. Logan, M. Kroumbi, Bargon, *J. Mol. Cryst. Liq. Cryst.* **1982**, 83, 265.

[24] S. Asavapiriliyanont, G.K. Chandler, G. A. Gunawardena, D. Pletcher, *J. Electroanal Chem.* **1984**, 177, 229.

[25] J. Hepel, S. Bruckenstein, M. Hepel, M. Ditzler, *Microchem. J.* **1997**, 55, 179.

[26] C. Ehrenbeck, K. Juttneret, K. Scott, *Electrochim. Acta* **1996**, 41, 511.

[27] M. Hepel, *Electrochim. Acta* **1996**, 41, 63.

[28] S. Gaspar, L. Muresan, A. Patrut, I.. C. Popescu, C. Brett, A. M. Oliveira-Brett, *Anal. Chim. Acta* **1999**, 385, 111.

[29] M. Tolgyesi, A. Szucs, C. Visy, M. Novak, *Electrochim. Acta* **1995**, 40,1127.

[30] S. Suematsu, Y. Oura, H. Tsujimoto, H. Kanno, K. Naoi et A.R. Hillman, *Electrochim. Acta* **2000**, 45, 3813.

[31] S. Bruckenstein, K. Brzezinska et A.R. Hillman, *Electrochim. Acta* **2000**, 45, 3801.

[32] K. Kontturi, L. Murtomaki, P. Pentti et G. Sundholm, *Synth. Met.* **1998**, 92, 179.

[33] M. Hepel, Z. Xingmin, R. Stephenson, S. Perkins et M. Ditzler, *Microchem. J.* **1997**, 56,79.

[34] J. F. Bergamini, S. Aeiyach ; K. L. Chane-Ching, M. Jouini, J. C. Lacroix, P.C. Lacaze, P. Hourquebie, F. Jousse et L. Olmedo, *J. Chim. Phys.* **1998**, 95, 1498.

[35] A. C. Partridge, C. B. Milestone, C. O. Too et G. G. Wallace, *J. Membr. Sci.* **1999**, 152, 61.

[36] T. F. Otero et H. J. Grande, *Colloids Surf. A* **1998**, 134, 85.

[37] C. Deslouis, M. M. Musiani, B. Tribollet, Z. V. Vardeny et A. J. Epstein, *Synth. Met.* **1997**, **84**, 827.

[38] C. Deslouis, T. El-Moustafid, M. M. Musiani, B. Tribollet et J. Vereecken, *Electrochim. Acta* **1996**, 41, 1343.

[39] C. Ehrenbeck, K. Juttner, S. Ludwig, G. Paasch et W. J. Lorenz, *Electrochim. Acta* **1998**, 43, 2781.

[40] L. S. Van-Dyke et C. R. Martin, *Langmuir* **1990**, 6, 1118.

[41] C. Ehrenbeck, K. Juttner, B. Tribollet et M. Vorotyntsev, *Electrochim. Acta* **1996**, 41, 1815.

[42] T. Sata, *Sensors Actuators B* **1995**, 23, 63.

[43] J. Bobacka, G. Zhiqiang, A. Ivaska et A. Lewenstam, *J. Electroanal. Chem.* **1994**, 368, 33.

[44] S. Dong, G. Che, *Talanta* **1991**, 38, 111.

[45] B. Sun, P. G. Fitsch, *Electroanalysis* **1997**, 9, 494.

[46] Z. Lu, Z. Sun, S. Dong, *Electroanalysis* **1989**, 1, 271.

[47] R. S. Hutchins et L. G. Bachas, *Anal. Chem.* **1995**, 67, 1654

[48] A. Michalska et A. Lewenstam, *Anal. Chim. Acta* **2000, 406,** 159.

[49] Z. Gao, J. Bobacka, A. Lewenstram, A. Ivaska, *Electrochim. Acta* **1994**, 39, 755.

[50] T. Okada, H. Hayashi, K. Hiratani, H. Sugihara et N. Kozhizaki, *Analyst* **1991**, 116, 923.

[51] A. Lewenstam, A. Michalska et A. Ivaska, *Chem. Anal.* **1995**, 40, 587.

[52] T. Blaz, J. Migdalski et A. Lewenstam, *Talanta* **2000**, 52, 319.

[53] J. Tamm, A. Alumaa, A. Hallik et V. Sammelselg, *J. Electroanal. Chem.* **1998**, 448, 25.

[54] A. Codagan, G. Zhiqiang, A. Lewenstam, A. Ivaska et D. Diamond, *Anal. Chem.* **1992**, 64, 2496.

[55] R. E. Gyurcsanyi, A. S. Nyback, K. Toth; G. Nagy et A. Ivaska, *Analyst* **1998**, 123, 1339.

[56] T. Momma, S. Komaba, M. Yamamoto, T. Osaka, S. A. Yamauchi D'amico et C. Di-Natale, *Sensors Actuators* B **1995**, 25, 724.

[57] T. Momma, M. Yamamoto, S. Komaba et T. Osaka, *J. Electroanal. Chem.* **1996**, 407, 91.

[58] S. Komaba, J. Arakawa, M. Seyama, T. Osaka, I. Satoh et S. Nakamura, *Talanta* **1998**,46, 1293.

[59] I. Poels, L. J. Nagels, *Anal. Chim. Acta* **1999**, 401, 21.

[60] K. S. Kwok, K. P. Siu et K. C. Ho, *J. Electroanal. Chem.* **1994**, 367, 115.

[61] D. Centonze, A. Guerrieri, C. Malitesta, F. Palmisano et P. G. Zambonin, *Fresenius J. Anal. Chem.* **1992**, 342, 729.

[62] A. Kitani, N. Kasyu et K. Sasaki, *Electrochim. Acta* **1994**, 39, 7.

[63] T. Miyasaka, Y. Yoshimi et K. Sakai, *J. Chem. Eng. Japan* **1998**, 31, 29.

[64] F. Palmisano, A. Guerrieri, M. Quinto et P. G. Zambonin *Anal. Chem.* **1995**, 67, 1005.

[65] E. C. Hernandez, A. Witkowski, S. Daunert, L. G. Bachas et O. S. Wolfbeis, *Mikrochim. Acta* **1995**, 121, 63.

[66] T. Tatsuma, T. Watanabe, S. Tatsuma et T. Watanabe, *Anal. Chem.* **1994**, 66, 290.

[67] V. Lvovich et A. Scheeline, *Anal. Chem.* **1997**, 69, 454.

[68] T. Tatsuma, M. Gondaira et T. Watanabe, *Anal. Chem.* **1992**, 64, 1183.

[69] G. F. Khan, E. Kobatake, Y. Ikariyama et M. Aizawa *Anal. Chim. Acta* **1993**, 281, 527.

[70] W. Somers, R. T. M. Van-Den-Dool; G. A. H De-Jong, J. A. Jongejan; J. A. Duine et J. P. Van-Der-Lugt, *Biotech. Tech.* **1994**, 8, 407.

[71] S. Kuwabata, C. R. Martin, *Anal. Chem.* **1994**, 66, 2757.

[72] T. Hianik, Z. Cervenanska, T. Krawczynski-Vel-Krawczyk et M. Snejdarkova, *Mater. Sci. Eng. C* **1998**, 5, 301.

[73] D. Tsamouras, E. Dalas, S. Sakkopoulos et E. Vitoratos, *Phys. Scripta* **1993**, 48, 521.

[74] I. Lahdesmaki, A. Lewenstam et A. Ivaska, *Talanta* **1996**, 43, 125.

[75] M. E. G. Lyons, C. H. Lyons, C. Fitzgerald et P. N. Bartlett, *J. Electroanal. Chem.* **1994**, 365, 29.

[76] Y. J. Yuan, Z. Huijun, G. G. Wallace et S. B. Adeloju, *Electrochem. Comm.* **2000**, 2, 27.

[77] G. Zhiqiang et A. Ivaska , *Anal. Chim. Acta* **1993**, 284, 393.

[78] F. Palmisano, C. Malitesta, D. Centonze et P. G. Zambonin , *Anal. Chem.* **1995**, 67, 2207.

[79] G. Zhiqiang, Z. Minxian et C. Beshen, *J. Electroanal. Chem.* **1994**, 373, 141.

[80] P. Audebert , P. Aldebert et M. Pineri , *Synth. Met.* **1989**, 32, 1.

[81] F. Endres et G. Schwitzgebel, *Synth. Met.* **1997**, 88, 73.

[82] H. Zhao, W. E. Price et G. G. Wallace, *J. Membr. Sci.* **1998**, 148, 161.

[83] M. Nikpour, H. Chaouk, A. Mau, J. C. Dong et G. Wallace, *Synth. Met.* **1999**, 99, 121.

[84] M. Bleha, V. Kudela, E. Y. Rosova, G. A. Polotskaya, A. G. Kozlov et G. K. Elyashevich, *Eur. Polym. J.* **1999**, 35, 613.

[85] G. Tishchenko, E. Rosova, G. K. Elyashevich et M. Bleha, *Chem. Eng. J.* **2000**, 79, 211.

[86] G. A. Tishchenko, M. Bleha, E. Y. Rozova et G. K. El-Yashevich, *Polym. Sci. A* **2000**, 42, 230.

[87] M. Morita, *Macromol. Chem. Phys.* **1999**, 200, 2139.

[88] D. Zhou, C.O. Too, G. G. Wallace, A. M. Hodges et A. W. H. Mau, *React. Funct. Polym.* **2000**, 45, 217.

[89] T. Sata, *J. Phys. Chem.* **1993**, 97, 6920.

[90] T. Sata, *J. Membr. Sci.* **1992**, 66, 289.

[91] T Sata, *Electrochim. Acta.* **1994**, 39, 131.

[92] T Sata, *J. Membr. Sci.* **1993**, 82, 247.

[93] T Sata, S. Ogura et F. Kishimoto, *J. Membr. Sci.* **1993**, 84, 259.

[94] T. Sata, T. Funakoshi; K. Akai, *Macromol.* **1996**, 29, 4029.

[95] T. Sata, *J. Membr. Sci.* **1992**, 72, 43.

[96] E. Dalas, *Solid State Comm.* **1991**, 71, 63.

[97] H. Zhao, W. E. Price, C. O. Too, G. G. Wallace et D. Zhou , *J. Membr. Sci.* **1996**, 119, 199.

[98] H. Zhao, W. E. Price et G. G. Wallace, *J. Electroanal Chem.* **1992**, 334, 111.

[99] H. Zhao, W. E. Price et G. G. Wallace, *Polymer* **1993**, 34, 16.

[100] H. Zhao, W. E. Price et G. G Wallace. , *J. Membr. Sci.* **1994**, 87, 47.

[101] H. Zhao, W. E. Price, P. R. Teasdale et G. G. Wallace, *React. Polym.* **1994**, 23, 213.

[102] P. Gros, T. Gibson, A. Bergel et M. Comtat, *J. Electroanal. Chem.* **1997**, 437,125.

[103] A. Mirmohseni, W. E. Price et C. G. Wallace, *J. Membr. Sci.* **1995**, 100, 239.

[104] K. Kamada, J. Kamo, A. Motonaga, T. Iwasaki et H. Hosokawa, *Polym. J.* **1994**, 26, 141.

[105] M. Zhou , M. Persin et J. Sarrazin, *J. Appl. Electrochem.*, **1996**, 26, 711.

[106] M. Zhou, M. Persin et J. Sarrazin, *J. Membr. Sci.* **1996**, 117, 303.

[107] M. Zhou, private communication.