

On the behaviour of polyimide ion-selective membranes in electrolyte solutions

E. EFTIMIE TOTU*, E. RUSE, I. DIACONU, R. GÎRDEA

Department of Analytical and Instrumental Analysis, Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Str. Polizu 1 - 4, Bucharest, Romania

The work presented in this paper was realized using the polyimide obtained through the polycondensation of the pyromellitic dianhydride with 4, 4' - diaminophenyl ether. Polyimide based polymeric membranes were characterized as regards the a.c. impedance and electrochemical analyses. The experiments put in evidence the influence of the membrane composition on the electrochemical answer of the sensor. Also, it was put in evidence the action of the electrolyte solutions upon the selective membranes. Through impedance analysis it was possible to show that the water from the aqueous electrolyte solution acts not only as a plasticizer for the polymeric matrix, but it also exists as absorbed water on the membrane surface. Meanwhile, it was concluded that the addition of the lipophilic agent in the selective membrane composition results in membranes with higher dielectric constant. The dielectric constant of the polymeric matrix of the ion-selective devices based on neutral carriers has an important influence on selectivity.

(Received November 12, 2009; accepted November 23, 2009)

Keywords: Polyimide polymeric matrix, Plasticizer, Plasticizing effect of electrolyte, a.c. Impedance analysis, Lipophilic additive

1. Introduction

Applications of the a.c. impedance spectroscopy is varied and suppose characterization of materials, their behavior in different surroundings and an aid in the fabrication process to improve materials. This method is also used to determine relationship between material's electrical properties and other physical, chemical and even mechanical properties of materials. Impedance spectroscopy (IS) is a general term that subsumes the small-signal measurement of the linear electrical response of a material of interest (including electrode effects) and the subsequent analysis of the response to yield useful information about the physicochemical properties of the system. Analysis is generally carried out in the frequency domain, although measurements are sometimes made in the time domain and then Fourier transformed to the frequency domain.

The impedance spectra contain features which are directly related to the microstructure. An important aspect of microstructures studies by impedance spectroscopy has been to optimize electrical conductivity for use in solid state electrochemical devices, as are the chemical sensors. The preliminary experiments were focused on the preparation of new ion-selective membranes to be used for improved ion-selective electrodes (ISE). There were obtained calcium – selective membranes whose properties were established through experiments at ISE level [1, 2]. Subsequently, such membranes were used to realize calcium-selective microdevices as ISFET. In order to use ion selective membranes as active material for chemical microsensors, a high importance is given to the width of the membrane whose charge depends on the dielectrical constant of the membrane, ϵ , and also on the concentration

of the co-ordination positions and the valence [1]. Although the membranes under study present a cationic specificity, the presence of the lipophilic anions in sample could cause significant alterations from the Nernstian answer for potential due to a competitive reaction to the main complexation / decomplexion analyte reaction. As consequence, the anions concentration in membrane is increasing and it could overcome the concentration of the anion charges which result in a decrease of the cationic permselectivity and an increase in membrane's conductance. Precise information on the variation of the dielectrical constant of the polymeric matrix could be obtained using the impedance spectroscopy method [4]. Such a.c. impedance experiments put in evidence not only the action manner of the aqueous solution on the selective membrane behaviour, but it also permits the determination of the electrical characteristics of the membranes. These characteristics are useful when establishing the correct composition of a functional selective membrane [1].

2. Experimental

Lately, p-chloro-phenyl borate is incorporated in membranes based on the property of neutral carriers to reduce the interference due to the lipophilic anions present in sample. In fact, an increased concentration of the anionic positions present in the organic phase is increasing the membrane permselectivity for cations due to its reduced solubility in water.

Within the characteristic temperatures range for the common usage of the selective membranes, polyimide is a vitreous material. Therefore it is necessary to add a suitable plasticizer. As polyimide is not compatible with

the plasticizers commonly used (oNPOE, DOS, DOA), the chemical compounds able to form suitable ion-selective polyimide membranes were dimethylphthalate (DMP); diethylene glycol dibenzoate (DGD) and phenylglycidylether (FGE) [2]. Their beneficial effect on polyimide membrane was put in evidence by the decrease of the glass transition point (T_g) [5, 6]. Depending on the nature and quantity of the used plasticizer the T_g value reached 9°C for the best performing selective membrane (60–66% plasticizer content).

The highest difficulty in handling the membranes' compositions consisted in the atmospheric water absorption following the high hygroscopicity of polyimide. Therefore, the study of the behavior of such polyimide selective membranes in electrolyte solutions proved to be important in order to establish the most suitable experimental conditions.

Throughout this work it was used as polyimide variety the synthesized polyimide starting from polyamic acid in order to compare the results of this study with those previously obtained [1, 2, 6, 7]. The plasticizer used to obtain the selective membranes was diethylene glycol dibenzoate – DGD, (Aldrich), which is a compound compatible with the polyimide [2]. All chemicals used were of analytical grade purchased from Fluka or Aldrich.

The polymer preparation supposed two stages: synthesis of polyamic acid and its subsequent imidization through thermal treatment [5]. The polyamic acid resulted from the dianhydride and aromatic diamine condensation. The dianhydride was kept in dry conditions and the diamine was used after its re-crystallization from 2 – propanol. The solvent, N, N' dimethylformamide (DMF), was used as received being kept and handled under nitrogen.

The studied membranes were obtained by dissolving the polyimide in 25% anhydrous dimethylformamide (Aldrich) and DGD as plasticizer. The selective membrane compositions were as stated in our previous works [1, 2]: electroactive material – the ionophore, plasticizer, lipophilic agent [potassium tetrakis (p-chlorophenyl) borate], and polymeric support – polyimide. There was used deionised water. The calcium ionophore was ETH 129 (Fluka). The exposure in aqueous electrolyte solution was done in CaCl_2 10^{-2} M for 48 hours.

The a.c. impedance studies were performed on Parstat 2273, Advanced Electrochemical System, Princeton Applied Research using a four electrode cell at room temperature. The soaking solution in cell was an aqueous CaCl_2 10^{-2} M solution to which a small amount of LiCl was added to assure the adequate conductivity of the solution and to maintain the stability of the silver / silver chloride reference electrodes used [4]. The experiments were performed over a frequency range of 10^6 – 0.1 Hz at 10 mV amplitude. Ten points per decade of frequency were collected going from high to low frequency. The impedance measurements were taken after equilibrating the cell typically for 2 – 2.5 hours.

3. Results and discussion

The polyamic acid was prepared at a final concentration of 11–15 %, by slowly adding under continuous stirring of a stoichiometric quantity of dianhydride into a diamine solution in DMF. The polymer was synthesized in a quantity of 5 -10 grams. The reaction took place into a dry atmosphere (N_2 purge). The solution was mixed up to 12 hours with an additional heating up to 80°C . The mixing level has to be adjusted according to the continuously modifying viscosity of the polymer.

A 25% solution of the obtained polyamic acid in DMF was deposited onto a glass slide and dry under nitrogen purge in order to obtain a homogeneous film. This film was further heated up to 300°C in order to escape of the water formed during the imidization reaction. The finally obtained polyimide is insoluble. This thermal conversion reaction was studied in our previous works [5, 6]. Also, the change of the polyamic acid into polyimide through thermal treatment was put in evidence by help of FT – IR analysis following the changes occurred in the compounds' spectra as reported in our early work [7].

The thermally treated polyamic acid film presented the characteristics of the insoluble imides structure. The data previously recorded showed that the imidization took place completely: the absorption due to the amide type bonds ($2865 - 3100$, approx. 1655 and approx. 1540 cm^{-1}) are under the detection limit, while the absorption due to the imidic type bonds are strongly present (approx. 1785 and 1720 cm^{-1}) [7]. Only the presence of a low intensity signal at 1620 cm^{-1} could be assigned to a rest of untransformed polyamic acid in polyimide by the thermal treatment.

Let consider a plasticized polyimide membrane with no ionophore present but with anionic sites and hydrogen counter ions ($\sim 10^{-7}\text{ mol/dm}^3$). On exposing the membrane, from lower to higher concentration solutions of calcium chloride (an equitransferent salt), since the concentration of anionic sites in the membrane is much greater than that of the calcium ions, hydrogen ions (in very low concentrations) are transferred to the bathing solution. This leads to a boundary potential at each interface which draws the potassium ions in to the membrane in higher concentrations (than the hydrogen ions). The anions in the membrane prevent chloride ions entering, thus cation permselectivity is created [8]. This effect, known as the Donnan Exclusion Principle, is the exclusion of ions of one charge, here anions, from the membrane. On addition of an ionophore to the membrane (ETH 129), calcium ions are more easily extracted into the membrane. As consequence, it results a lower boundary potential, E_B , at the interface and thus there is less exclusion of the free anions from the bathing solution. Hence, Donnan Exclusion Principle fails more easily in membranes with a good ionophore. This phenomenon is also known as Donnan Breakdown or Co-ion Exclusion Failure.

The behaviour of electrochemical sensors will vary depending on the resistance or the impedance of the membranes. From electrochemical studies over various

ion-sensors using selective membranes it came out that there are few electrical characteristics requested for a functional membrane. In this sense, it is desirable to work with a selective membrane with reduced bulk resistance which would signify a high value of the dielectrical constant and also to present a high value for conductivity.

The a.c. impedance experiments done in this work are based on the supposition that within the used frequency range ($10^6 - 10^{-1}$ Hz), the selective membrane behaves as a parallel circuit formed by a resistance and a capacitance. Applying the impedance data there were calculated the capacitances and then the dielectrical constant of the membranes whose value could help on deciding upon the functionality of an ion-selective membrane. Using the data from the impedance spectra it is possible to calculate the geometrical capacitance [9], and further it is possible to calculate the dielectrical constant of the membrane. In our experiments, the surface was of 1.50 cm^2 , and the membrane width was of 0.1 cm . The dielectrical constant of the membrane was evaluated against composition. The impedance spectra were analyzed supposing that within the used frequency range ($10^5 - 10^{-1}$ Hz), the ion-selective membrane behaves as a parallel circuit formed by a capacitance ($C_g = \epsilon A/d$) and a resistance ($R_b = d / \sigma A$) where A is the membrane area, d is the width, ϵ is the dielectrical constant and σ is the dielectrical conductivity of the membrane.

The initial polyimide films resistance of 10^8 Ohms is indicating the uniformity and excellent resistivity of the polyimide simple membrane. However, for the selective membranes obtained a decrease of impedance in the lower frequency region (10 to 10^{-2} Hz) was detected after the conditioning of the selective membranes, Figure 1. The presence of the ionic components with selective membrane proved to be beneficial, because the membrane resistance is reduced considerably.

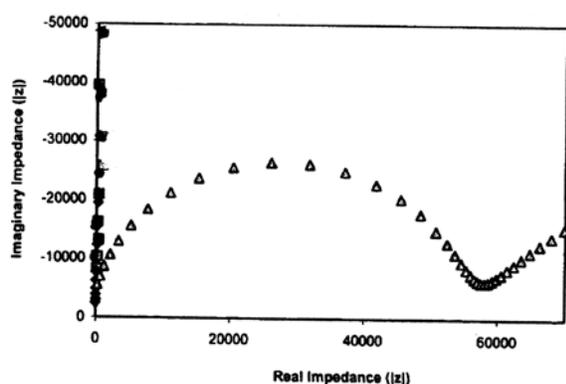


Fig. 1. Typical a.c. impedance spectra in Nyquist complex plot after exposure of the polyimide selective membrane in electrolyte solution (Δ); with \square and \circ it is presented the behaviour of the initial simple polyimide membrane with and without conditioning.

As shown in Table 1, the value of the dielectrical constant increased and consequently the bulk membrane resistance decreased when lipophilic agent (KTpCIPB) was added. This issue becomes very important for the microelectrodes case. Thus, incorporating in the ion-selective organic phase the p-chloro-phenyl borate as additive, this could be essential for the design of a functional microelectrode based on neutral carriers, showing a rapid response time. By realizing high concentrations of the anionic charges within membrane, there are facilitated the interfacial cations exchange reactions and it is significantly reduced the surface resistance.

Table 1. Variation of the dielectric constant for composition with and without additive.

Membrane composition	Dielectric Constant, ϵ_r
PI / DGD	32.06
PI / DGD / KTpCIPB	51.40

In order to assure an efficient salt dissociation the polyimide polymeric film has to present a high value of the dielectrical constant. Experimentally it was shown that a membrane with a higher dielectrical constant presents a satisfactory electrochemical behaviour against the divalent ions. Higher value for the dielectrical constant is obtained for compositions of the polyimide membrane with 60 % plasticizer content. The compositions with plasticizer content lower than 35% are not mechanically resistant, becoming brittle.

The variation presented in table 1 was expected for the functional selective membranes as the plasticizer content is very high (over 50%), and as consequence the value of the dielectrical constant of the membranes are close to that of the plasticizer (for DGD the dielectrical constant being 31.69). The further evaluation of the membrane's dielectrical constant after its conditioning for longer period of time (72 hours) did not put in evidence any ϵ_r variation.

Also, the conductivity of the selective membranes, σ , could be determined from the membrane resistance expression [4] using the a.c. impedance data. In this sense, the used plasticizer has a particular importance because it could modify the value of the membrane conductivity within the temperature range used for electrochemical determinations. This could be explained if it is considered a competition between the increase of the ionic mobility and the increase of the dissociation degree of the salt – lipophilic agent, KTpCIPB.

The experimental data were used to calculate the conductivity of various membranes as shown in Table 2. The improvement of the ionic conductivity when the plasticizer is added could be explained by the compatibility of the plasticizer with the polymeric matrix, resulting in a uniform conductive medium.

Table 2. Variation of the conductivity for polyimide membranes using diethylene glycol dibenzoate (DGD) as plasticizer.

Plasticizer concentrations in membrane composition	Conductivity $\times 10^9$ ($\Omega^{-1}\text{cm}^{-1}$)	
	No addition of KTpCIPB	Addition of - KTpCIPB
15%	0.23	15.21
20%	6.40	19.08
30%	8.50	32.31
35%	8.80	38.05
40%	7.10	33.23
50%	5.50	48.80
60%	3.95	57.29

As consequence, the number of the charged carriers increases through the dissociation of the ionic pairs. For comparison there were computed the conductivities for polyimide membranes without lipophilic agent and with lipophilic agent in different proportions. From the data obtained it was noticed an increasing by three magnitude orders for the conductivity when compared with the polyimide membrane without lipophilic agent.

For a concentration of 40% plasticizer in the polymeric matrix, it could be noticed a sharp variation for the conductivity value, similar with the behaviour of the membrane obtained from commercial polyimide – for 50% DGD content [2], which is an unexpected behaviour because the ionic mobility should increase when increasing the plasticizer concentration in polymer. In Table 3 there are presented the main electrochemical characteristics of the obtained membranes.

Table 3. Main electrochemical characteristics of polyimide membranes.

Membrane composition	Resistance (M Ω / cm)	Capacitance C_g (pF cm^{-1})	Dielectric constant
PI / DGD /	0.6000	175.0	32.06
PI / DGD / KTpCIPB	0.0770	270.0	51.40

The bulk resistance of the polyimide membrane is significantly improved when added the lipophilic agent, KTpCIPB, reaching a value of 77 k Ω . This value is a bit larger than the bulk resistance obtained for the membranes based on commercially available polyimide [2].

The water's influence on the plasticized polyimide membranes was followed up by help of a.c. impedance investigations performed both on "dry" membranes and on the conditioned (for 48 h) membrane using aqueous solutions of electrolyte. Such measurements put in evidence the increase of the conductivities values for the wet membranes, which could be associated with the incorporated water level. The behavior of the polyimide membranes when exposed to electrolyte solutions is due to a plasticizing action in the presence of water and not to a hydrolysis reaction. Also, there was noticed a change of the resistance of the film's surface only by a magnitude order when exposing in water the membranes for 10 days,

when compared with a membrane exposed for only 24 hours. It is known that the surface resistance is modified by 3 magnitude orders when exposing to water mixed polymeric films – polyimide – amide. The important variation of the resistance could be explained by an accumulation of some polar products resulting from hydrolysis.

4. Conclusions

The impedance spectroscopy technique proved again to be a useful procedure to evaluate and monitor the interfacial phenomena of polymeric membranes. The experiments performed proved the possibility to establish an optimum composition for the selective membranes using the a.c. impedance studies by help of the specific parameters as dielectrical constant, bulk resistance and conductivity. The results obtained showed that incorporating 60% DGD in polyimide matrix it could be obtained the best balance between the improvement of the membrane's conductivity and the mechanical integrity of the membrane. The resistance of the polyimide selective membrane was significantly improved when added the lipophilic agent. Also, by help of the a.c. impedance study performed on polyimide membranes it was proved that the water acts as a plasticizer for the polymeric matrix. In the case of the plasticized polyimide membranes, the reduced variation of the film's resistance is caused only by the adsorption of water and not by a hydrolysis reaction.

Acknowledgments

The work was financially supported by the research contract CNMP 62-074/ 2008.

References

- [1] E. Totu, A.K. Covington, *Analyst* **121**, 1811 (1996).
- [2] E. Totu, E. Ruse, A. M. Josceanu, *Anali di Chimica* **96**(3-4), 237 (2006).
- [3] R. D. Armstrong, G. Horvai, *Electrochimica Acta* **35**, 1 (1991).
- [4] E. Totu, E. Ruse, C. Luca, *Rev. Roum. Chim.* **51**(5), 331 (2000).
- [5] E. Eftimie Totu, *Rev. Chim.* **57**(9), 2006.
- [6] E. Eftimie Totu, E. Ruse, I. Diaconu, *Optoelectron. Adv. Mater. – Rapid Comm.* **3**(8), 808 (2009).
- [7] E. Eftimie Totu, E. Ruse, R. Gardea, A. Grigorescu, *Optoelectron. Adv. Mater. – Rapid Comm.* **2**(7), 442 (2008).
- [8] F. G. Helfferich, *Ion Exchange*, Ed. Courier Dover Publications, 135, 1995.
- [9] R. P. Buck, K. Toth, E. Graf, G. Horvai, E. Pungor, J. *Electroanal. Chem.* **223**, 51 (1987).
- [10] A. J Bard, L. R. Faulkner, *Electrochimie: principes, methodes et applications*, Ed. Masson, 1983.

*Corresponding author: eugenia.eftimie@et-consulting.ro