



HAL
open science

Prime importance of the supporting electrolyte in the realization of molecularly imprinted polymers

Meriem Mokni, Zouhour Mazouz, Ghada Attia, Najla Fourati, Chouki Zerrouki, Ali Othmane, Asma Omezzine, Ali Bouslama

► To cite this version:

Meriem Mokni, Zouhour Mazouz, Ghada Attia, Najla Fourati, Chouki Zerrouki, et al.. Prime importance of the supporting electrolyte in the realization of molecularly imprinted polymers. MOL2NET 2018, International Conference on Multidisciplinary Sciences, 4th edition, Jan 2018, Paris, France. pp.5888, 10.3390/mol2net-04-05888 . hal-04490353

HAL Id: hal-04490353

<https://hal.science/hal-04490353>

Submitted on 5 Mar 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Prime importance of the supporting electrolyte in the realization of molecularly imprinted polymers

M. Mokni^{1,2*}, Z. Mazouz^{3,4}, G. Attia¹, N. Fourati¹, C. Zerrouki¹,
A. Othmane⁴, A. Omezzine², A. Bouslema², R. Kalfat³

¹ SATIE, UMR CNRS 8029, Cnam, 292 rue Saint Martin, 75003, Paris, France. E-Mails: fourati@cnam.fr (N.F.); zerrouki@cnam.fr (C. Z.); ghada.attia@lecnam.net (G.A.)

² Service de Biochimie, Hôpital Universitaire Sahloul, 4011, Sousse, Tunisia. E-Mails: asmaomezzine2@gmail.com (A.O.); ali.bouslama@rns.tn (A.B.)

³ LMTA, INRAP, Sidi Thabet 2020, Tunisia. E-Mails: mazouz.zouhour645@gmail.com (Z.M.); rafik.kalfat@gmail.com (R.K.)

⁴ LIMA, Faculté de Médecine de Monastir, Université de Monastir, 5000, Av. Avicenne Monastir, Tunisia. E-Mail: ali.othmane54@gmail.com (A.O.)

* Author to whom correspondence should be addressed; E-Mail: mokni.meriem@hotmail.fr
Tel.: 00 33 1 40 27 21 64

Abstract:

This study concerns the highlighting of the role of supporting electrolyte in the realization of stable and reproducible molecular imprinted polymer (MIP), as it is one of the key elements which can affect the MIP's morphology, and thus the corresponding electrochemical response. Here we have designed a MIP with pyrrole, as functional monomer, and prostate specific antigen (PSA) as template. Several electrolytes were tested at a fixed concentration of 0,16 M: phosphate buffer solution (PBS), NaCl, KCl and LiClO₄ in PBS solutions. Square wave voltammetry was investigated to get information about the most appropriate electrolyte. The follow up of variations of PSA peak currents indicates that the MIPs realized in LiClO₄ give the better electrochemical response. The morphological analyses of the electropolymerized MIPs, investigated with atomic force microscopy, confirm the electrochemical results and permitted to highlight the role of anions and cations in MIP's design.

Keywords: Molecularly imprinted polymer; polypyrrole; supporting electrolyte; square wave voltammetry; Atomic force microscopy

Mol2Net YouTube channel: <http://bit.do/mol2net-tube>

YouTube link: *please, paste here the link to your personal YouTube video, if any.*

1. Introduction

Molecularly imprinted polymers (MIPs) are attracting considerable attention nowadays, due to their "relative ease" of concept and the possibility of their use in several applications varying from drug release, protein and DNA sensing, to quenchers in SERS experiments. Molecular imprinting principle is based on the

creation of specific and selective cavities in a 3D-polymeric network, which are complementary in size and shape of target species, providing thus interaction points and a coordination sphere around the template molecule.

Among the large panel of functional monomers, we have chosen pyrrole, due to its biocompatibility, the possibility of its use at neutral pH in either aqueous or organic solvents, and mainly the relative ease of its polymerization. Because of the rapidity of polypyrrole (PPy) electropolymerization, several synthesis mechanisms were proposed in literature [1]. The most consensual one is that presented by Genies et al [2]: the electropolymerization is initiated by

2. Results and Discussion

Previous studies have demonstrated that the supporting electrolyte play an important role in the PPy electropolymerization process [4-5]. The most appropriate one corresponds generally to a compromise between several parameters, mainly the solubility, the electrochemical stability and the interaction with reaction intermediate.

Here, we have chosen to investigate four electrolytes at a fixed concentration of 0,16 M: NaCl, KCl and LiClO₄ (in PBS solution) and PBS.

Square wave voltammetry was carried out to follow up the oxidation peak of PSA.

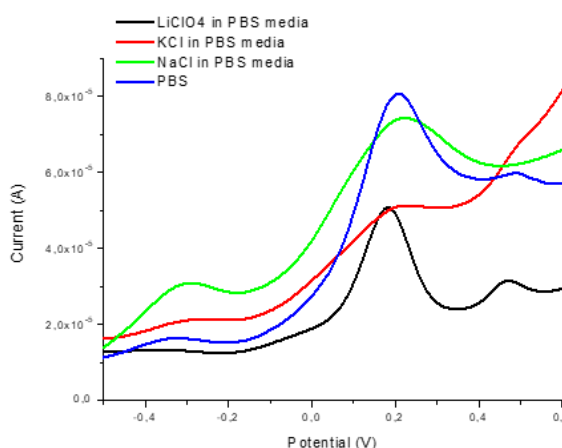


Figure 1. Characterization by square wave voltammetry of MIPs with different supporting electrolytes.

Square wave voltammograms presented in Figure. 1 indicate that the oxidation peak of PSA is more intense in a PBS solution, but it is less resolved than that of LiClO₄ in PBS.

Broad peaks were recorded in KCl/PBS and NaCl/PBS supporting electrolytes. This result is in good agreement with the previous publications relating the role of counter ions in the process of electropolymerization and electrical conductivity

the generation of radical cations monomers at the surface of the electrode and then followed by a rapid growth of the PPy chain. However, there are many factors that can interfere in the polymer synthesis such as solvent nature, pH, temperature and mainly supporting electrolyte [3].

This study is devoted to highlighting the role of the supporting electrolyte in the design of PPy molecular imprinted polymer. Prostate Specific Antigen was investigated as template molecule.

of the PPy [4-7]. LiClO₄ in PBS was thus chosen to realize the PSA/MIPs.

NaCl, KCl and LiClO₄ molecularly imprinted polymers topographies were investigated by means of atomic force microscopy. Figure. 2 shows an obvious difference between the realized MIPs. In fact, MIPs realized with ClO₄⁻ ions are more uniform than those made with Cl⁻ small ion. These results confirm the role of counterion in the structure regularity and morphology of PPy films [8-9].

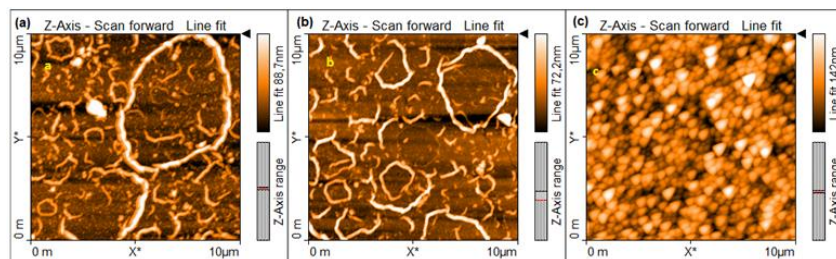


Figure 2: AFM images corresponding to MIPs realized in PBS solutions containing a) NaCl, b) KCl and c) LiClO₄ supporting electrolytes

The comparison between Figure 2a and 2b indicates that the cations can also play a role in MIPs morphology. In fact, and despite the fact that NaCl and KCl based MIPs present “rings like structures”, those of NaCl are more regular and are regularly distributed on the surface. Note that this is not a salt effect accumulated on surfaces, as the electrodes were copiously rinsed with DI water prior to AFM analysis. This results very interesting, as electrochemical studies concerns generally only the influence of the nature of the counter ion.

3. Materials and Methods

Sulfuric acid (H₂SO₄, 95%), hydrogen peroxide (H₂O₂, 30%), lithium perchlorate (LiClO₄), sodium chloride (NaCl), potassium chloride (KCl) and phosphate buffer solution (PBS) were purchased from Sigma Aldrich and used as received. Pyrrole (Py) was purified before its use by filtering through basic alumina column and stored in dark at 4°C.

Prior to any measurement, a drop of a piranha solution (98% H₂SO₄ / 30% H₂O₂ 1:1 V/V) was deposited, during 20 min, on the gold sensing areas of the gold electrodes. The substrates were then copiously rinsed with deionized double distilled water, then with ethanol before being dried under ambient air.

Before MIP deposition, a thin barrier PPy layer was electropolymerized by CA at a constant potential of 1.05 V vs SCE during 2 s.

4. Conclusions

This study permits to highlight the role of the supporting electrolyte on both electrochemical response and structural morphology of a molecular imprinted polymer. Square wave voltammetry results indicate that LiClO₄ (in a PBS solution) is the most appropriate supporting electrolyte. AFM topographic studies showed

MIPs were then prepared by CA at the fixed potential of 1.05 V vs SCE during 7s with the following concentrations: [PPy] = 10⁻² M, [PSA] = 5x 10⁻⁶ M and [supporting electrolyte] = 0.16 M.

Chronoamperometry and Square wave voltammetry measurements were carried out with a CHI 650E potentiostat with the following parameters: increment = 5 mV, amplitude = 25 mV, frequency = 25 Hz, and sensitivity = 1.10⁻⁴. A three-electrodes configuration was used: a gold electrode, a saturated calomel electrode (SCE) and a platinum wire as the working, the reference and the auxiliary electrodes respectively.

AFM measurements were investigated with a Nanosurf easyScan 2 Flexsystem.

that varying the counterion (ClO₄⁻ vs Cl⁻) modify the MIPs morphology, and that ClO₄⁻ anions permitted to obtain more uniform microscopic structure than Cl⁻ ones.

Further investigations are necessary to establish the cations effects on the electrical conductivity of PPy based MIPs.

Acknowledgments

The authors would like to thank "Campus France" for the financial support of this work through the project PHC Utique n°16G0808.

Conflicts of Interest

The authors declare no conflict of interest

References and Notes

1. Sadki, S., et al., The mechanisms of pyrrole electropolymerization. *Chemical Society Reviews*, 2000. 29: p. 283-293.
2. Genies, E. M., Bidan, G., Diaz, A. F. Spectroelectrochemical study of polypyrrole films, *J. Electroanal. Chem.*, 1983, 149, 101.
3. Ansari, R., Polypyrrole conducting electroactive polymers: synthesis and stability studies. *Journal of Chemistry*, 2006. 3(4): p. 186-201.
4. Yamaura, M., T. Hagiwara, and K. Iwata, Enhancement of electrical conductivity of polypyrrole film by stretching: Counter ion effect. *Synthetic Metals*, 1988. 26(3): p. 209-224.
5. Vorotyntsev, M.A., E. Vieil, and J. Heinze, Charging process in polypyrrole films: effect of ion association. *Journal of Electroanalytical Chemistry*, 1998. 450(1): p. 121-141.
6. Tamm, J., et al., Study of the properties of electrodeposited polypyrrole films. *Russian Journal of Electrochemistry*, 2004. 40(3): p. 344-348.

7. Warren, L.F. and D.P. Anderson, Polypyrrole films from aqueous electrolytes the effect of anions upon order. *Journal of the Electrochemical Society*, 1987. 134(1): p. 101-105.
8. Kupila, E.-L. and J. Kankare, Influence of electrode pretreatment, counter anions and additives on the electropolymerization of pyrrole in aqueous solutions. *Synthetic Metals*, 1995. 74(3): p. 241-249.
9. Paramo-García, U., Ibanez, J. G., and Batina, N. AFM Analysis of Polypyrrole Films Synthesized in the Presence of Selected Doping Agents. *Int. J. Electrochem. Sci*, 2013(8): p. 2656-2669.

Notes:

MDPI do not released one specific template for Sciforum conference. Consequently, this is not official template released by MDPI. In principle, the papers may be presented without specific format. However, the chairperson and the secretariat of the conference decided to create this template to give homogeneity to Mol2Net works. As is, this template should be used only for Mol2Net conference. Please, do not use this template for MDPI journals. Please, delete these notes before saving your final version. Type of the Paper (Proceeding, Letter, Expert Opinion, Communication, etc.). MDPI generates doi upon author request.

YouTube link: this option is only for those authors with welcome videos and/or oral presentations, plenary conferences uploaded to Mol2Net YouTube site.

Reference list: *We recommend the use of reference management software to prepare the references list (e.g., Endnote, <http://endnote.com/styles/MDPI.ens>).*

© 2018 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions defined by MDPI AG, the publisher of the Sciforum.net platform. Sciforum papers authors the copyright to their scholarly works. Hence, by submitting a paper to this conference, you retain the copyright, but you grant MDPI AG the non-exclusive and unrevocable license right to publish this paper online on the Sciforum.net platform. This means you can easily submit your paper to any scientific journal at a later stage and transfer the copyright to its publisher (if required by that publisher). (<http://sciforum.net/about>).