



## Short communication

## Development of a redox polymer based on poly(2-hydroxyethyl methacrylate) for disposable amperometric sensors

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## ABSTRACT

Membranes based on poly(2-hydroxyethyl methacrylate), chemically modified with ferrocene functionalities, are proposed as novel coatings for the development of disposable amperometric sensors. They are mass-produced on an inert support through an UV photo-induced polymerization, forming self-standing films that can be transferred on an electrode surface. Thanks to the characteristic of the functionalized methacrylate matrix to rapidly and reversibly swell by incorporation of large amounts of water, the ferrocene moieties are in intimate contact with the electrolytic solution. They can activate effective electrocatalytic processes that can be exploited in the field of amperometric sensing. The performance of the methacrylate coating with respect to the determination of hydroquinone benchmark analyte has been tested both in a static solution and in a flux cell.

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## 1. Introduction

Amperometric sensors are acknowledged to be very efficient devices for food, environmental, clinical analyses and for process control. In the development of effective electrode systems, electrode coatings play the most meaningful role, imparting the device specific physico-chemical properties and corresponding analytical peculiarities. In particular, the acquisition of electrocatalytic activity is often sought, in order to detect target analytes at low potential values, where redox processes due to the solvent medium and to additional electroactive species present in the solution are absent [1]. To reach this goal, a suitable redox mediator is often fixed on the electrode [2]. In this context, a critical aspect is represented by the poor stability of the anchoring and by the time consuming procedures often required for the periodical renewal of the electrode functionality. An effective approach to overcome both these problems is represented by the use of disposable electrode coatings that covalently bond the redox mediator.

Poly(2-hydroxyethyl methacrylate) (pHEMA) forms a hydrogel in water. Self-standing films can be easily obtained through UV-induced photo-polymerization of 2-hydroxyethyl methacrylate (HEMA) in the presence of a photo-initiator. Molecules possessing

a suitable functionality can be included by co-polymerization, stably linking the functional group to the pHEMA matrix. By following this approach, functionalized pHEMA membranes were successfully used for the development of an optical sensor for pH determination [3]. In that case, the sensing element, namely fluorescein, was linked to a methacrylate monomer in order to be stably bonded to pHEMA membrane; the sensor quickly responded to variable solution pH, in a flow cell system.

pHEMA-based thin films have been also proposed as coatings for amperometric biosensors [4]: a solid film was directly obtained on the electrode surface by photo-polymerization of a drop of HEMA and vinylferrocene mixture. The resulting modified electrode was tested as an enzymatic biosensor for the determination of glucose. Furthermore, a different biocatalytic sensor was obtained by simply including ferrocene in the pHEMA material during UV-polymerization process [5].

It is however evident that the number of applications of pHEMA in the field of sensing, and in particular of amperometric sensing, is quite low.

In the present study, ferrocenylmethyl methacrylate (Fc-MMA) was co-polymerized with HEMA in order to build up a redox polymer in which the ferrocene/ferricinium ion (Fc/Fc<sup>+</sup>) redox couple is covalently bonded to the polymer chains. The resulting membranes consist of self-standing films that can be mass-produced by UV photo-induced polymerization on an inert support and easily transferred onto the

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electrode surface just before use. Thanks to the capability to swell once in contact with water, the Fc redox active residues inside the membrane are in intimate contact with the electrolytic solution: the  $\text{Fc}/\text{Fc}^+$  redox couple acts as the redox mediator with respect to proper substrates in solution. In the present article, as a proof of concept, the electrode system was tested as a sensor for hydroquinone (HQ) determination, both in static and in flux electrochemical cells.

## 2. Material and methods

### 2.1. Synthesis of the pHEMA based membranes

All reagents used for the synthesis of pHEMA-based membranes were from Sigma-Aldrich. Basically, two different starting solutions have been prepared. In a first one, 0.50 g (3.8 mmol) of HEMA, 0.01 g (3.3  $\mu\text{mol}$ ) of Fc-MMA (95% pure), 0.30 g of water and 0.03 g (0.2 mmol) of photo-initiator, namely 2-hydroxy-2-methylpropiophenone, were mixed in a sonicator for 20 min. In a second one, 0.050 g (0.46 mmol) of hydrophilic sodium methacrylate and 0.01 g (5.0  $\mu\text{mol}$ ) of a bifunctional crosslinking agent, namely ethylene glycol dimethacrylate, were added to the former recipe, and the amount of water was increased to 0.50 g. In both cases, a number of similar membranes, possessing 0.39 mm mean thickness (measured by a Borletti MDE1 digital micrometer) were simultaneously obtained: drops (6  $\mu\text{l}$  each) of pristine solution were deposited onto a polypropylene foil and exposed to UV light (Dymax Light-Curing Flood-Lamp System Model 5000, 4.9  $\text{W}/\text{cm}^2$ ) for a time suitable to achieve solidification. In particular, 180 and 240 s time lengths were adopted for the first and the second mixture, leading to  $\text{p(HEMA-Fc)}^*$  (two-component copolymer) and  $\text{p(HEMA-Fc)}$  (four-component copolymer), respectively. In order to evidence the effect induced by the presence of Fc moieties, membranes have been also synthesized with similar pristine solutions, in absence of Fc-MMA, obtaining pure  $\text{p(HEMA)}^*$  and  $\text{p(HEMA)}$ , respectively.

### 2.2. Analytical tests

Dry  $\text{p(HEMA)}^*$  and  $\text{p(HEMA-Fc)}^*$  membranes were positioned on the electrode surface and wet with a drop of water, inducing stable adhesion to electrode substrate.

$\text{p(HEMA)}$  and  $\text{p(HEMA-Fc)}$  membranes were conditioned before use by immersion in water for at least 10 min. In this step Fc-MMA not included in the co-polymer chain is released in solution, whereas the volume of the membranes increases of about ten times. The wet membranes were then placed on a Pt electrode and fixed by an O-ring and an external cap in order to achieve best fixing of the coating.

Modified electrodes were tested in a 0.1 M phosphate buffer solution (PBS) at  $\text{pH} = 7.0$ . Known amounts of HQ were added, in order to define the performance of the sensing system. Cyclic voltammetry (CV) was the voltammetric technique chosen, sweeping the potential from  $-0.3$  to  $+0.6$  V at  $0.02 \text{ Vs}^{-1}$  potential scan rate.

Tests were also performed in a flux cell (0.35 ml/min flux rate) in a configuration typical of flow injection analysis: 100  $\mu\text{l}$  of a solution containing HQ at given concentrations was periodically added to the cell through a loop.

### 2.3. Instrumentation

All electrochemical measurements were performed with an Autolab PGSTAT12 (Ecochemie) potentiostat/galvanostat. A 2 mm diameter Pt disk (Metrohm, Herisau, Switzerland) was used as the working electrode; a GC rod was the auxiliary electrode and an aqueous  $\text{Ag}/\text{AgCl}$ , 3 M KCl (Metrohm) was the reference. The working electrode was polished subsequently with 0.05  $\mu\text{m}$  alumina powder, then rinsed with distilled water in an ultrasonic bath before use.

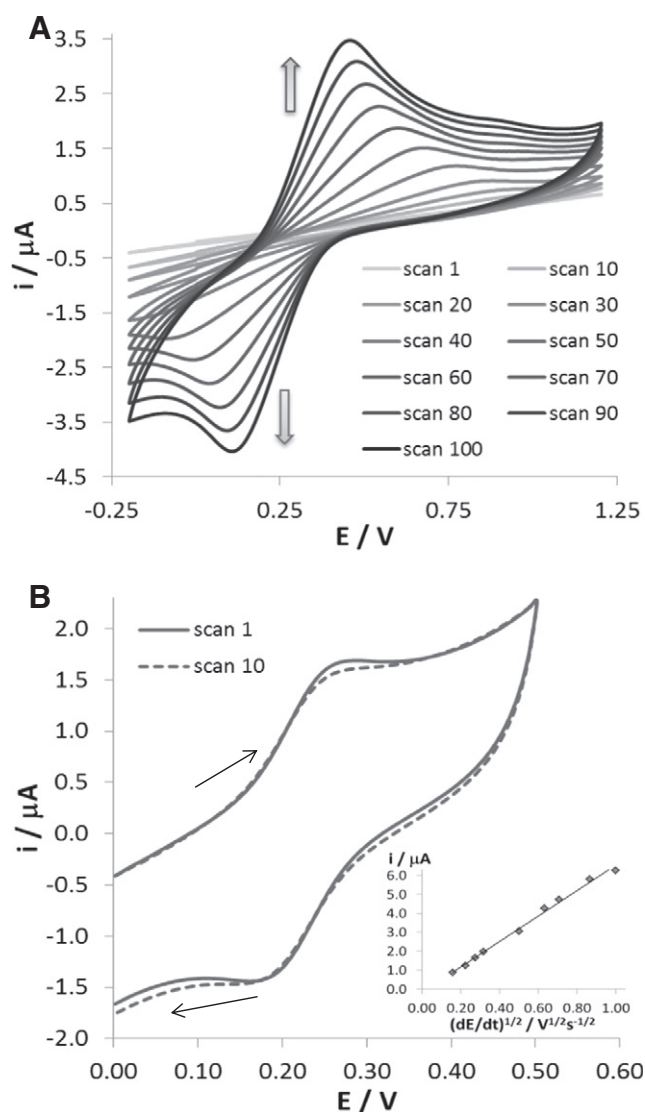
Thermogravimetric analyses on dry and wet membranes were performed with Netzsch STA 309 simultaneous TGA-DTA analyzer, in static air, on 19.1 and 5.0 mg of sample, respectively, in a Pt crucible;  $5^\circ\text{C}/\text{min}$  heating rate till  $800^\circ\text{C}$ .

ICP-MS analyses were performed with a HR/MC/ICP-MS Neptune (Thermo Fisher Scientific) after complete mineralization of the membranes in an UltraClave microwave digester (Milestone).

XRF analyses have been performed on the conditioned membrane, with a Bruker axs analyzer.

## 3. Results and discussion

$\text{p(HEMA-Fc)}^*$  membranes have been firstly tested in PBS, leading to record the typical voltammogram reported in Fig. 1A. The increasing height of the anodic–cathodic peak system in subsequent potential cycles, ascribed to the  $\text{Fc}/\text{Fc}^+$  moieties bonded to the polymer chains [4,6–10], indicates the progressive swelling of the membrane due to the inclusion of counterions from the solution to compensate the charges brought by the  $\text{Fc}^+$  residues formed. Water molecules also



**Fig. 1.** Different CV scans of A)  $\text{p(HEMA-Fc)}^*$  and B)  $\text{p(HEMA-Fc)}$  modified Pt electrodes in PBS;  $v = 0.10$  and  $0.05 \text{ Vs}^{-1}$ , respectively. Grey arrows in A indicate the evolution of the voltammogram scan by scan. Inset in B reports the plot of current peak values vs. square root of the potential scan rate.

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