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Electrochemically switchable polypyrrole coated membranes

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ABSTRACT

A method for coating membranes with polypyrrole (PPy) has been developed. Different membranes, such as microfiltration as well as ion exchanger membranes have been coated with PPy to yield electrical conductivity of the membranes.

The coated membranes have been investigated by cyclic voltammetry and scanning electron microscopy and their permeability and permselectivity have been tested. The results show that PPy can be tailored as cation or anion exchanger and its porosity can be controlled to avoid any impairment of the membrane by the polymer layer. These PPy coated membranes can be applied as electrochemically switchable, functionalised membranes with controllabel and variable separation properties.

1. Introduction

Membranes are prevalent in numerous applications concerning chemical, environmental and medicinal engineering and will further gain weight in technical processes. However, the separation properties of membranes are limited and specified to fit certain applications.

Aim of this study is the development of functionalised membranes with electrochemically switchable separation properties. Such switchable membranes would be favourable compared to conventional membranes, because their separation properties can be altered to fit different separation requirements. Withal the separation properties could be adjusted during the separation process without the need to discontinue the process and to exchange the membranes.

Conventional separation membranes are electrically non-conductive. To gain electrochemical switchability, the membranes are coated with the conducting polymer polypyrrole (PPy).

The properties of conducting polymers can be controlled by their electrical polarisation [1–3] porosity can be adjusted as well as the change of volume of the coating [4] to control, e.g., the pore diameter of the membrane.

The ion exchange properties of conducting polymers depend on preparation conditions, polymer thickness [5], type and size of counterions [6–12] as well as type and size of ions in the surrounding electrolyte [5,10,13,14]. Polyprrole can be tailored as anion or cation exchanger by the entrapment of different counterions [15–17], and has been applied as electrochemically switchable ion exchanger for water softening [18–20].

By controlling these properties, the PPy coatings can be tailored to provide membrane attributes as, e.g., permeability, permselectivity, wettability for certain applications and additionally the membrane properties can be electrochemically switched to fit the requirements of different membrane processes.

Furthermore the scaling and fouling of a membrane can be reduced by electrochemical polarisation of PPy coated membranes [21,22] and PPy embedded on the surface of Nafion membranes has been investigated for fuel cell applications [23–25].

2. Experimental

To coat the membranes, an arrangement of two half cells made of glass has been developed (Fig. 1). The membranes were fixed horizontal between the half cells, the lower compartment of the cell was filled with the monomer solution and the upper compartment was filled with an oxidant (Fig. 1A). The pyrrole monomer diffused through the membrane towards the upper cell and was polymerised by the oxidant as a PPy coating on the membrane (Fig. 1B). Electrolyte ions as PSS anions or $NaSO_4^{2-}$ anions were incorporated into the PPy as counterions.

Pyrrole monomer (Aldrich, distilled before use) and oxidant ($Na_2S_2O_8$ or $FeCl_3$) as well as additional electrolyte (NaPSS (Aldrich), Na_2SO_4 or NaCl) were used as 0.1 M solutions prepared from ultrapure water (PURELAB Ultra, ELGA).

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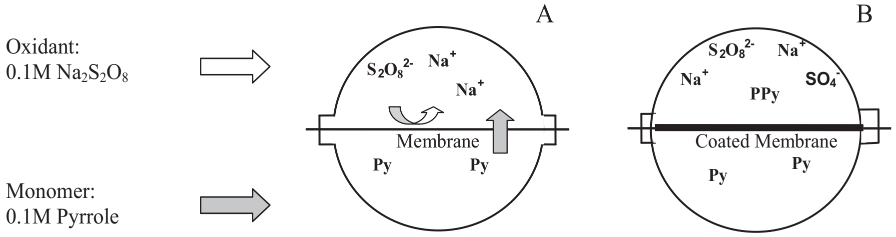

Fig. 1. Scheme of the coating procedure of a membrane with PPy. (A) Filling of the cell and (B) deposition of the PPy layer.

Microfiltration membranes (Millipore: Durapore 0.22 μm; symmetrical membrane made of polyvinylidenflouride (PVDF) and Biomax 0.22 μm; asymmetrical membrane made of polyethersulfone (PES)) as well as anion exchanger membranes (Fumatech: FAB, made of poly(2,6-dimethylphenylenoxid) with quarternairy ammonium ions) were coated with polypyrrole (PPy). The membranes were used dry without pretreatement and the coated membranes have been stored in ultrapure water.

The morphology of the coated membranes was examined with a scanning electron microscope (SEM) XL-40, Philips. Cross-sections were prepared by freezing and breaking the membranes in liquid nitrogen. The samples were sputtered with a gold layer.

Electrochemical activity of the coated membranes was characterised by cyclic voltammograms (CV) recorded in 0.1 M Na_2SO_4 with potentiostat EG&G 263A. Membrane disks with 1.5 cm diameter were fixed in a teflon frame with a Pt-wire as electrical contact and a Pt-net as counter electrode.

Permselectivity was investigated by measuring membrane potentials of the membranes between two half cells filled with KCl solutions of different concentrations.

Reference electrode was an Ag/AgCl-elektrode (SE 21, Sensortechnik Meinsberg GmbH) with 211 mV vs. standard hydrogen electrode (SHE) in a luggin capillary.

Permeability was tested with ultrapure water at a pressure of 2 bar on membrane disks with 2.5 cm diameter fixed in a filter arrangement.

The electrochemically switchable ion exchanger behavior was tested with 0.005 M $CaCl_2$ solution at flow rates of 2–3 ml/min on membrane disks with 2.5 cm diameter fixed in a filter arrangement with a Pt-wire as electrical contact, a Pt-wire as a quasi-reference and a Pt-net as counter electrode. Polarisation was controlled by Potentiostat EG&G 263A. Ca concentration in the filtrate was determined by atomic absoprtion spectroscopy (AAS) with Perkin-Elmer 1100B Atomic Absorption Spectrophotometer.

3. Results and discussion

SEM investigation of a cross-section of a PPy coated membrane in Fig. 2 illustrates, that PPy polymerises only on one side of the membrane. During polymerisation this side was turned to the oxidant. Further the layer does not polymerise only on top of the membrane but grows deep into the membrane (Fig. 2). This is favourable concerning the adherence and mechanical stability of the PPy coating. The infiltration of the membrane by the polymer depends on the duration of polymerisation; with increasing polymerisation time the PPy penetrates deeper into the membrane.

Electrochemical activity of the PPy coating correlates also to the polymerisation duration, respectivly the thickness of the PPy coating. Fig. 3 shows CV of a noncoated membrane and membranes coated with 15 and 30 min polymerisation. The current density increases with increasing duration of the polymerisation due to increasing thickness of the coating. Further the increasing current reveals, that not only the PPy on the surface of the membrane but also the PPy penetrated deep into the membrane contributes to the electrochemical activity.

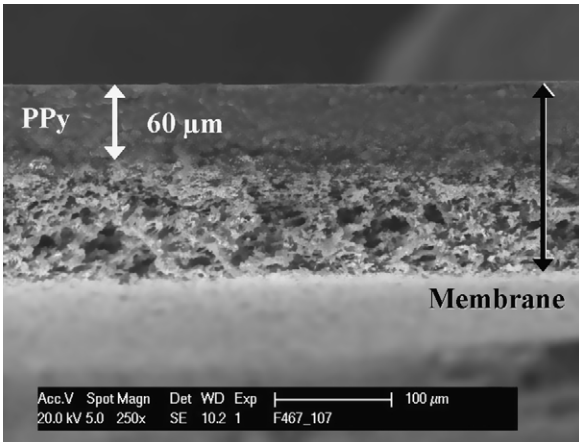

Fig. 2. SEM: cross-section of a PPy coated microfiltration membrane (PES, 0.22 μm) after 15 min polymerisation.

Electrochemical activity also depends on the counterions incorporated into the PPy coating during polymerisation. Fig. 4 shows CV of membranes coated with equal duration of polymerisation in the presence of different counterions. The PPy coating with $SO_4{}^{2-}$ counterions yields higher currrent densities than the coating with PSS ions.

The counterions even have an influence on the permeability of the coated membranes. The results of permeation tests in Fig. 5 reveal, that the flow rate of the coated membranes is lowered compared to the uncoated membrane. This is caused by the polymerisation of PPy in the pores of the membranes which leads to a reduction of the pore diameter or even blockage of the pores. Further Fig. 5 shows that the flow rate of the coated membranes

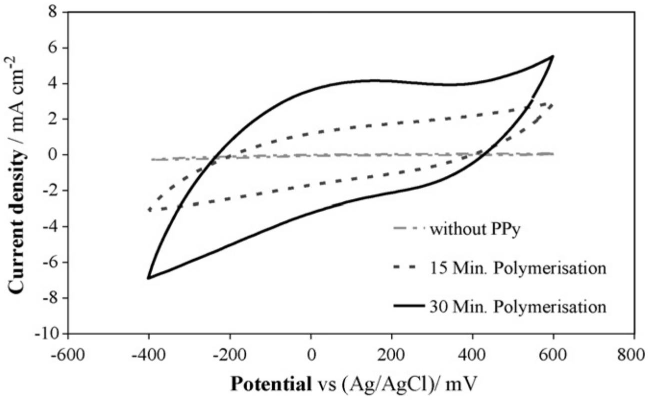

Fig. 3. CV: microfiltration membrane (PES, 0.22 μm) without PPy coating and with PPy coating after 15 and 30 min polymerisation (polymerisation from 0.1 M Py and 0.1 M NaPSS, oxidant 0.1 M $Na_2S_2O_8$). 0.1 M Na_2SO_4, $\nu = 10\,mV\ s^{-1}$.