Electrochemically switchable membranes

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Subject

A method for coating membranes with the conducting polymer polypyrrole (PPy) has been developed and different membranes such as ion exchanger membranes, filtration membranes and reverse osmosis membranes have been coated.

The conducting polymer layers can be tailored as cation- or anion exchangers and their porosity can be controlled to avoid any impairment of the membrane by the polymer coating.

Due to the properties of conducting polymers the coated membranes can be applied as electrochemically switchable membranes with controllable separation properties.

Furthermore membrane scaling or fouling can be reduced by electrochemical switching of the coated membranes.

Formation of the polymer coating

The membrane is fixed in a cell. One compartment of the cell is filled with the pyrrole monomer solution (Py) and the other compartment is filled with an oxidant. The pyrrole monomer diffuses through the membrane (Fig.1A) and is polymerised by the oxidant (e.g. $Na_2S_2O_8$) as a PPy coating on the membrane (Fig.1B).

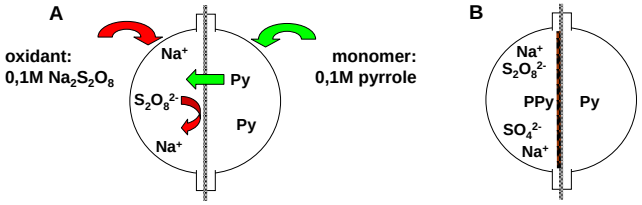

Fig.1: Coating of a membrane with PPy.
A: Filling of the cell, B: Deposition of the PPy layer.

Characterisation of the polymer coating

Scanning electron microscopy (SEM) pictures and cyclic voltammograms (CV) reveal the PPy layers on microfiltration membranes and their electrochemical activity (Fig.2). The thickness, respectively the penetration depth, of the PPy coatings and their electrochemical activity increases with increasing duration of polymerisation.

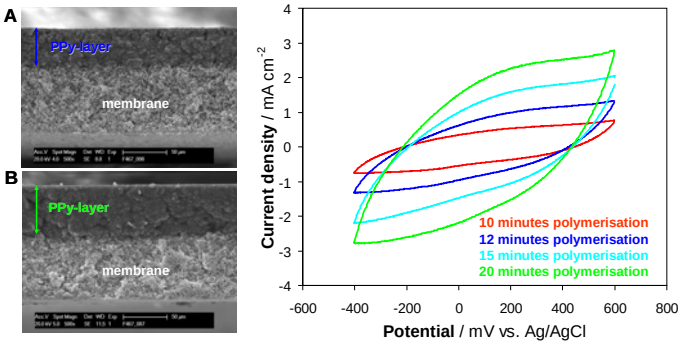

Fig.2: SEM: Cross-section of a PPy coated microfiltration membrane after 12 minutes (A) and 20 minutes (B) polymerisation
CV: Increasing current density with increasing polymerisation time.
Microfiltration membrane of polyvinylidenefluoride (PVDF), 0.22µm.

The permeability of the PPy coated membranes is decreased by the polymer layer (Fig.3). The porosity of the coating is affected by the counterions which are incorporated into the PPy. Coatings with SO_4^{2-}-counterions allow higher flow rates than coatings with PSS-counterions (Fig.3).

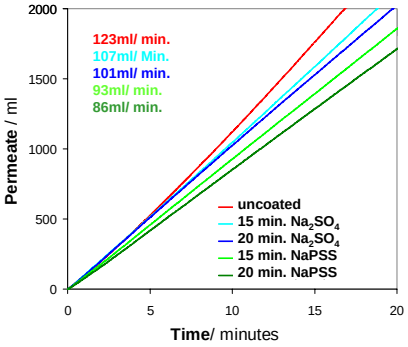

Fig.3:
Flow rate at 2 bar for ultrapure water of uncoated and PPy coated microfiltration membranes with different counterions: SO_4^{2-} or PSS (PSS=Polystyrensulfonate).

Microfiltration membrane of polyethersulfone (PES), 0.22µm.

Also permselectivity can be controlled and altered by the PPy coating. A PPy coating with Cl^--counterions improves the permselectivity of an anion exchanger membrane, whereas the anion exchanger membrane coated with a PPy layer with PSS-counterions loses its permselectivity (Fig.4).

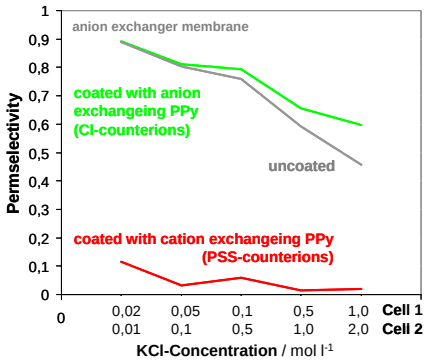

Fig.4:
Permselectivity of an uncoated and a PPy coated anion exchanger membrane with Cl^--counterions or PSS-counterions (PSS=Polystyrensulfonate).

Anion exchanger membrane of poly(2,6-dimethylphenylenoxid) with quaternary ammonium ions.

Application as electrochemically switchable ion exchanger

A microfiltration membrane coated with PPy with PSS-counterions works as an electrochemically switchable cation exchanger membrane (Fig.5).
Cathodic polarisation yields in a decrease of the Ca-concentration in the filtrate due to adsorption of Ca-cations by the PPy/PSS coating. During anodic polarisation the Ca-concentration in the filtrate is increasing due to desorption of Ca-cations from the PPy/PSS coating.

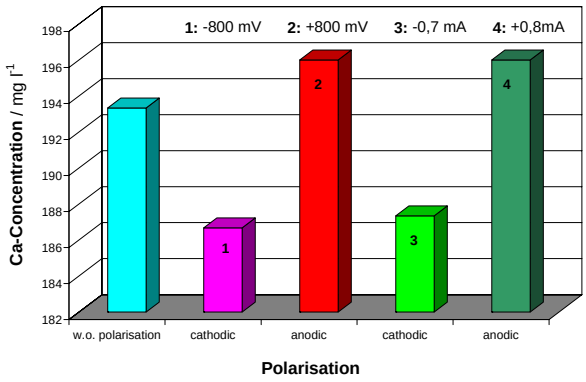

Fig.5: Ca-concentration in a filtrate passed a PVDF membrane (0,22 µm) coated with PPy with PSS-counterions (PPy/PSS) in dependence on galvanostatic or potentiostatic (vs. Ag/AgCl) cathodic (-800 mV or -0,7 mA cm^{-2}) or anodic polarisation (+800 mV or +0,8 mA cm^{-2}).

These coated membranes can be applied as electrochemically switchable membranes with controllable separation properties. Furthermore fouling caused by microorganisms can be reduced by electrochemical switching of the coated membranes (patent EP 1777250).