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Preparation of thin film composite membranes with polyamide film on hydrophilic supports

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ABSTRACT

The interest in osmotically driven processes such as pressure retarded osmosis (PRO) has increased during the past decade. The synthesis of new membranes specifically designed for the process is essential for the development of these technologies. Conventional TFC have a relatively hydrophobic support layer e.g., polysulfone. However, a more hydrophilic support layer is desirable in osmotically driven processes as such supports would give better water flux, less internal concentration polarization (ICP) and less fouling. In the current project it was demonstrated that it is possible to coat a hydrophilic support membrane given there are enough functional/reactive groups on the surface of the support membrane. This is achieved by reacting the support with polyfunctional acid chlorides in a reaction step prior to interfacial polymerization (IP). In this way, covalent bonds between the support and the active layer are formed and the composite will be stabilized. Hydrolysed cellulose acetate CA membranes have been coated with a polyamide (PA) layer by this modified IP method. These membranes displayed a salt rejection up to 97%, and water fluxes from 7.6×10^{-7} to 4.7×10^{-6} $m^3/m^2/s$ at 1.3×10^6 Pa differential pressures.

1. Introduction

1.1. General

The global energy demand is increasing as the world's population is growing and developing countries are becoming more industrialized. A significant portion of this energy is supplied through the use of fossil fuels such as coal, gas and oil. Anthropogenic climate change is a serious threat to modern society and there is an urgent need to search for alternative emission free energy sources [1–3]. The current global energy supply is still dominated by fossil fuels. Fossil fuels emit greenhouse gases and there is a common consensus among scientists that the emission of greenhouse gases is causing global warming. As an example, in 2008, 79% of the European gross inland energy consumption came from fossil fuels. However, the leaders of the European Union (EU) have agreed on legally binding national targets for increasing the share of renewable energy. The goal is to achieve a 20% share for renewable energy for the entire EU by 2020, compared with an 8.5% share in 2005 [4]. Pressure retarded osmosis (PRO) is a potential sustainable, non-polluting and renewable energy source. In a PRO process the free energy of mixing is converted to potential mechanical energy by the use of a semi-permeable membrane. In a fresh water/salt water system, the water flows from the fresh water side to the salt water side. A pressure builds up at the salt water side, and this can be used to run a turbine to generate electric power. The optimal operating pressure is 11–15 bars, enabling the generation of 1 MW/m^3 freshwater. The total global potential for osmotic power has been calculated to be 1655 TW h/year [5]. The concept of osmotic power was first introduced by Sidney Loeb in the 1970s [6,7]. Due to low prizes on electricity and poor membranes at the time, there were little or no commercial interests in developing PRO as an alternative energy source. However, in the late 1990s the Norwegian company Statkraft invested in a PRO project, resulting in the opening of the world's first PRO pilot plant November 2009 [8]. One of the major obstacles to the completion of a full scale osmotic power plant (OPP) has been the lack of a membrane designed specifically for the process. The membrane power performance, often referred to as the *power density* (W/m^2), is dependent on the water flux across the membrane. Therefore, a high water flux is important for an efficient PRO process. Most of the commercial available osmotic membranes today are reverse osmosis (RO) membranes, designed for pressure driven processes. Conventional seawater RO membranes are not suitable for use in osmotically driven membrane processes; the water flux obtained is too low. This is due to their hydrophobic and thick support layer and the hydrophobic interface between the active layer and the support. Membranes

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used in RO are either thin film composite (TFC) membranes or asymmetric cellulose based membranes like CA or cellulose triacetate (CTA). TFC membranes are generally considered to be the most promising membranes for osmotically driven processes. However, the synthesis of new membranes specifically designed for the process is essential for the commercialization of PRO. In order to establish PRO as a profitable renewable energy source, the power density of the membranes used must be in the range of 4–6 W/m^2 [5].

1.2. Challenges related to PRO versus RO membranes

Conventional RO TFC membranes are designed to withstand high pressure, and therefore have a thick support layer. This support layer is also relatively hydrophobic; a property that is not desirable in PRO. In RO the water first permeates the active layer by a solution-diffusion mechanism and then simply percolates through the pores of the support layer by hydraulic pressure. This implies that the porous support does not need to be fully wetted to ensure adequate water flux. However, in an osmotically driven membrane process the support layer must be fully wetted to ensure adequate water flux. The surface that the water meets when entering the active layer should preferably be hydrophilic. Vapour or air trapped in the pores might block the passage of water through the support layer. Reduced continuity of the water within the layer may exacerbate internal concentration polarization (ICP) and reduce the effective porosity [9,10]. A more hydrophilic support would most likely reduce or prevent this effect. In addition, hydrophilic CA membranes give less adsorptive fouling than other more hydrophobic membranes [11].

Most RO membranes display a flux decline during the initial period of a membrane separation process. The primary reason for this flux decline is external concentration polarization (ECP) on the salt solution side from where water is forced through the membrane. ECP is, however, considered to be reversible and can be controlled by promoting turbulence of the flow across the membrane, adjusting the shear rate, by the use of ultrasound or by the means of an electric field [12]. ICP is closely related to ECP, but it occurs exclusively in osmotically driven membrane processes. The concentration polarization occurs within the porous support layer and cannot be reduced by altering the shear rate and/or turbulence of flow across the membrane. Concentrative ICP occurs when the active layer of the membrane is facing the draw solution (Fig. 1). Salt diffusion through the active layer results in a higher C_{ICP} than C_F, resulting in a decrease in the transmembrane osmotic pressure. Dilutive ICP occurs when the active layer of the membrane is facing the feed solution. The water flux from the feed solution dilutes the draw solution in the porous support, resulting in a decrease in the transmembrane osmotic pressure (Fig. 1) [10,13].

The structure parameter (S) describes the inherent physical properties of an osmotic membrane. S is a function the thickness (x), the tortuosity (τ) and the porosity (φ) of the membrane:

$$S = \frac{x \times \tau}{\varphi} \tag{1}$$

A fully wetted hydrophilic support might increase effective porosity and therefore reduce the S value [14]. The desired value for the structure parameter in a PRO membrane is lower than 1500 μm. Standard RO membranes have a structure parameter ~10,000 μm [5,15].

Because the water passes through the membrane from the support side in PRO, fouling is also a more important issue in this process than in RO. In a real life PRO process, the feed from natural surface water will be of different quality than the feed used in laboratory research. Consequently, natural organic matter (NOM), calcium carbonate ($CaCO_3$) and microbial growth on the membrane will cause considerable fouling on the membranes used. The membrane materials and its properties are important factors for the membrane fouling characteristics. Polysulfone (PSf) membranes is a hydrophobic material and have a tendency to adsorptive fouling, while cellulose acetate (CA) membranes display little adsorptive fouling and are much easier to clean [11]. Several experiments have been performed at Sunndalsøra in Norway in order to investigate the fouling potential in PRO using typical Norwegian ocean water and surface water [16]. The membranes used were an asymmetric CA membrane manufactured by GKSS, Germany. Chemical cleaning of NOM and $CaCO_3$ were able to restore the initial flux for the membranes at 93% or higher. However, the effect of membrane cleaning was observed to decrease when repeating the cleaning. Periodical disinfection with 5 ppm free chlorine was observed to be sufficient in order to prevent microbial growth on the membranes during long term experiments with natural water sources [16]. Based on the findings referred here, and realizing the challenges related to make a high performance PRO membrane, the focus of the current work is to use a sufficiently, thin and hydrophilic support membrane and coat it with a very thin film of an active polyamide (PA) layer. Interfacial polymerization of PA on hydrophilic support is not trivial, as the active layer easily delaminates from the support, but was successfully achieved by Nilsen and Alsvik [17,18]. The most likely explanation for the delamination is that the layers in a conventional PA-TFC membrane are held together by adhesion forces. When the support becomes too hydrophilic, the adhesion forces are too weak to keep the layers together. Unfavorable

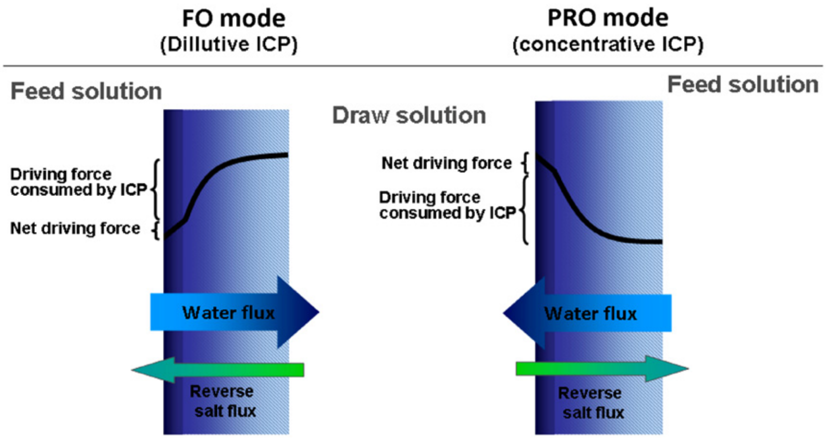

Fig. 1. Dilutive and concentrative internal concentration polarization in an osmotically driven process [10].