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Towards ultrathin polyaniline films for gas separation

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Abstract

A novel process has been developed to produce defect-free polyaniline-based composite membranes. These membranes consist of a thin polyaniline film (0.8–10.5 μm) and polyvinylidene difluoride (PVDF) as support material. The composite structure enhances flexibility and ease of handling of the material. This is demonstrated through tensile testing of the membranes.

The polyaniline composite membranes were subjected to gas permeability studies. Despite being prepared with a thickness of less than 1 μm the dense supported polyaniline maintained its previously reported intrinsic selectivity for different gases.

The novel fabrication process has the potential of producing nano scale membranes with much enhanced permeation rates.

Keywords: Gas separation; Polyaniline; Composite membranes; Submicron; Membrane preparation

1. Introduction

The concentration, purification and separation of gaseous mixtures are major problems in chemical industries. Membrane-based gas separation technologies first were commercialised in the 1980s when Air Products launched its Prism© membrane-based systems for hydrogen separation. With membrane-based separation systems offering an energy efficient alternative to other separation processes such as cryogenic, adsorptive and absorptive separation processes, the industry has grown into a US$ 150 million per year business. It is predicted that this figure will rise to US$ 760 million in 2020 [1]. For example, Koros and Mahajan [2] report that worldwide approximately 30% of the annual nitrogen gas production is firmly based on membrane separation processes.

The separation performance of membrane materials is usually described by the selectivity that can be achieved and by the permeability of the membrane material (in Barrer) which describes the flux that can be obtained (independent of pressure drop and membrane thickness). These two properties appear to be inversely related, that is if the permeability for a species is increased, the corresponding selectivity tends to decrease. There appears to be an upper bound for the performance of membranes (Robeson's upper limit, Robeson et al. [3,4]). However, this limit has shifted between 1980 and 1991 by a factor of 2 [5]. The separation performance of membranes is still gradually increasing, albeit at a slower rate.

It is not the scope of this contribution to provide a comprehensive review of the performance of membrane materials that are currently being investigated—however, it is important to address recent activities and innovations in the field in order to assess opportunities for future developments and to put the membrane material/system investigated in this contribution into context.

From an industrial point of view, permeability/flux and selectivity are only two issues to be dealt with when considering membrane separation processes. Other important factors include the cost per unit surface area (cost of fab-

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rication and materials) and the physical and chemical stability of the membrane against plasticising compounds that might be present in the gas phase. Polyaniline exhibits strong chemical stability against most solvent vapours, its separation performance is only affected to a small extent by plasticising gases such as CO_2. Of special interest for industrial applications are membrane-based gas separation processes for dehydration and the dewpoint reduction of natural and/or process gases [6] as well as the removal of volatile organic compounds (VOCs) [7–9] reports of a hybrid system, consisting of a membrane system (1st stage) and a PSA (pressure swing adsorption) unit (2nd stage). The membrane system is used to remove high concentrations of VOC and the following PSA step carries out the post processing to meet regulatory requirements. Oxygen enrichment for the combustion of low quality coal to enhance efficiency is of great importance, especially for Russia with its abundant sources of low quality coal [10]. For fuel cell powered vehicles and stationary fuel cell applications oxygen enrichment of air as well as hydrogen purification is of special interest [11]. For this purpose membranes with high separation factors and cocurrently high flux rates are required. The continuous and efficient operation of fuel cells requires strict control of the partial pressure of oxygen since this factor significantly influences the electrical power output. Current emphasis in this area is devoted to developing asymmetric membranes with ultrathin layers of dense, highly selective materials on top of an asymmetric support structure [12]. The membrane may consist of one material (selective layer and support are the same material) or may employ two or more materials in its fabrication. Manipulation of rheology and evaporation time/rate allow control of the development of porosity when casting flat sheet membranes through phase inversion [13–16]. The calculated apparent skin layer thickness in the above cases lies between 50 and 500 nm. This thickness allows for decent fluxes. The present paper describes a novel process whereby ultrathin (nano) dense membranes of polyaniline can be deposited on a porous support structure, thereby creating an asymmetric membrane.

Since the permeability of a compound through a dense selective film (membrane) is the product of its solubility and diffusivity in the material, an improvement of selectivity can only be achieved if either of these variables is manipulated and subsequently different for the two (or more) compounds to be separated. The diffusivity can be modified by changing and controlling for example the orientation of the polymer molecules that form the film. Again this can be achieved through appropriate inversion techniques whilst applying certain shear rates. This is probably most applicable to hollow fibre processing due to the intrinsic formation process of the fibre (spinning). Another method of changing diffusivities is to modify the void volume in the dense film by incorporating inorganic materials with large free volumes (e.g. silica aerogels) [17–19]. This leads to the formation of mixed matrix membranes. In these a reversal of selectivity can be induced whereby the increased void volume allows faster diffusion of larger molecules which on the other hand usually are more soluble in the membrane material.

In order to use solubility to affect selectivity, different membrane materials or surface treatments need to be considered. The ideal system would comprise of a membrane material which could be tailored by a simple doping process to suit the separation task. Polyaniline is one such material that, through doping, allows for significant changes in the solubility of gases, thereby changing the permeability and ultimately the selectivity.

Polyaniline is a dopable conjugated polymer like polypyrrole or polythiophene. Polyaniline can exist in various oxidation states characterised by the ratio of amine to imine nitrogen atoms [20]. Introducing anions into the polymer allows a change from the non-conducting isolator state ($>10^{-10}\,\Omega\,\mathrm{cm}$) to electronic conductivity ($<1\,\Omega$). Doping also causes significant changes to its gas transport properties. Rebattet et al. [21] showed, that doping of the membrane increases the sorption of polyaniline powder and the interaction energies to various gases and reported of polyargon–oxygen interactions as a mechanism for oxygen permeability.

In 1991 Anderson et al. [22] achieved highest selectivities for various gases by a controlled doping processes of polyaniline films. Not only the doping process itself was thought to cause these changes in selectivity but also structural modification was considered.

In order to increase the performance of polyaniline membranes (re. stability and selectivity), research has focussed on creating polyaniline/polyimide blends [23,24] stabilizing polyaniline layers with nylon support materials [25] or to create asymmetric PANi hollow fibers [26]. The difficulty of producing thin, stable, and defect-free polyaniline films is illustrated in Table 1 which gives a brief list of film thickness achieved. While self-supporting films are in the range of 10–100 μm, only supported polyaniline films can be prepared thinner than 10 μm.

This communication deals with a novel preparation process for the production of ultrathin, strong polyaniline membranes for enhanced gas permeation.

Table 1
Thickness of polyaniline films used for gas permeation tests

Publication, author	Thickness of polyaniline film (μm)
Chang et al. [28]	100
Conklin et al. [29]	50
Hachisuka et al. [14,15]	20–30
Rebattet et al. [21]	10–15
Lee et al. [25], on nylon support	5
Kuwabata and Charles [30], unsupported and on alumina support	20–30, 3–4
Present work: polyaniline/PVDF composite	0.8–8.4