



Effect of different metal *in situ* growing routes on the morphology and gas separation properties of polyetherimide/palladium nanocomposite asymmetric membranes



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ABSTRACT

Objective: Here we report on an innovative synthesis of polymer/palladium asymmetric membrane that allows a control of the membrane morphology, the specific location of *in situ* grown Pd nanoparticles within the membrane and significant enhancement of H₂ permeance values with respect to the reference polymer membrane.

Materials and method: Nanocomposite asymmetric films have been prepared from polyetherimide and palladium acetate for Pd amount ranging from 0 to 15 wt%. In this work, we have at first demonstrated that polyetherimide/palladium acetate membranes of different porous microstructures could be successfully prepared from a cononsolvent process. The influence of the composition of the PEI solution and of the cononsolvent immersion bath on the precursor membrane morphology was studied. Pd nanoparticles were then *in situ* grown within the membranes by two different post-treatments, an annealing treatment with a final step at 220 °C or a chemical treatment consisting in immersing the precursor membranes in a methanol/sodium borohydride solution.

Results: In this work, we have at first demonstrated that polyetherimide/palladium acetate membranes of different porous microstructures could be successfully prepared from a cononsolvent process. The structure and the repartition of the nanoparticles, determined from XRD and TEM characterizations, were discussed as a function of the *in situ* generation routes. The gas permeance was determined for H₂ and CO₂ and the ideal H₂/CO₂ selectivity factor was analysed for the two nanocomposite series. The nanocomposite membrane series prepared from the annealing post-treatment exhibited particularly interesting properties towards H₂ separation applications.

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1. Introduction

During the past decades, hydrogen has progressively become one of the most attractive source for energy. The emergence of a hydrogen-based economy is tightly related to necessity for efficient hydrogen production, safe and long-term hydrogen storage, transport and delivery from the production site to the end user and final use into energy conversion systems such as fuel cells. Interestingly, production of hydrogen can be performed from non-renewable resources (petroleum, coal, natural gas) as well as from renewable energy sources (biomass, biogas) [1–4]. However, in all cases, H₂ purification from other gases remains a challenging task. In this context, the separation process using gas separation membranes has been paid great attention as it offers less energy consumption, less environmental impact and ease of operation

[5–7]. Different membrane types such as inorganic membranes, metallic membranes or polymer membranes have been considered for this goal. Defect-free membranes have to exhibit low cost, no brittleness, high selectivity along with high hydrogen fluxes, resistance to poisoning and long operation lifetimes. Polymer membranes [8–11] hold an edge over the others due to the desired mechanical property and the flexibility to be processed. The separation of H₂ from other gases is obtained because of the extreme higher diffusion coefficient of H₂ relative to all the other molecules. However, the hydrogen permeation fluxes are generally limited in agreement with the upper bound trade-off curve. On the other hand, the rigid inorganic (carbon, molecular sieves, zeolites) or metallic (palladium or palladium alloys) materials are expected to exhibit more interesting permeability and selectivity properties. However, they have difficulties in forming continuous and defect free membranes and they are more expensive [12–15]. Association of designed polymer matrix with inorganic or metallic species represents then a promising alternative to the conventional

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monomaterial membranes. Mixed matrix composite membranes that are fabricated by encapsulating molecular sieves into polymer matrix have been extensively and intensively examined [16–22]. On the other hand, palladium nanoparticles have been more rarely combined with polymer matrices and dense membranes containing a homogeneous dispersion of the metal nanoparticles have been principally prepared [23–30]. Here we report on an innovative synthesis of glassy polymer/palladium asymmetric membrane that allows both a control of the membrane morphology and a specific location of *in situ* grown Pd nanoparticles within the membrane.

Glassy polymers are attractive materials to prepare membranes for gas separation. Commercially available polyetherimide (PEI), whose chemical structure is presented in Fig. 1 has several advantages as membrane material. It combines a good chemical and thermal stability with an easy processing ability.

The aromatic imide units provide stiffness and heat resistance, while the swivel groups such as $-O$ and $-C(CH_3)_2$ form flexible macromolecular chains that allow for good processability [31]. Moreover, dense PEI film exhibits high intrinsic selectivity for many gas pairs [32,33]. Although PEI has a lower gas permeability in comparison with other glassy polymers such as polyethersulfone, its higher intrinsic selectivities associated to its easy processing makes this polymer an attractive membrane material [34–36]. Indeed, the gas flux through the membrane can be increased by using a suitable preparation method that improves membrane morphology to obtain a high permeability without reducing membrane selectivity. Therefore, numerous studies have been focussed on the preparation of PEI asymmetric membranes or hollow fibre membranes by using the most usual techniques to prepare asymmetric porous structures such as: dry/wet phase inversion, phase inversion using Lewis acid:base complex solvents; and dual-bath methods [37–43]. Based on a study of the phase behaviour of PEI in mixtures of N-methyl-2-pyrrolidone (NMP) and methylene chloride (MC), Tao et al. evidenced that NMP and MC are solvents for PEI, respectively, but these two solvents mixed in appropriate volume fractions can also act as cononsolvent leading to a liquid–liquid demixing of PEI solution [44]. Therefore, depending on the composition of PEI solution, NMP and MC can play the roles of solvent and nonsolvent simultaneously. This cononsolvent approach was successfully used to prepare asymmetric pure PEI membranes with the aim to obtain tissue-engineering scaffold for bone regeneration [45].

During the past decades, a lot of attention has been paid on the preparation of porous or asymmetric polymer nanocomposite membranes. An extensive work has been focussed on the study of the formation of these membranes by adding preformed particles such as TiO_2 , SiO_2 , ZrO_2 , zeolites or Ag to the solution of the membrane-forming polymer (mainly polysulfone, polyvinylidene fluoride, cellulose acetate) [46–49]. By this route, the skin layer thickness as well as surface porosity of the skin was generally found to be highly dependent on the nanofiller type and content. An alternative way to prepare porous polymer nanocomposite membranes consists in *in situ* forming the nanoparticles during the membrane preparation. This strategy has already been applied to the formation of metal nanoparticles such as silver thanks to the chemical reduction of metal ions by a component of the casting

solution to obtain porous membrane with enhanced antibacterial properties [49,50]. Several studies have also been concerned with *in situ* grown Pd nanoparticles within polymer membranes. However except some studies [51], the main part of the work was focussed on dense membranes [23,24,28,29].

Three objectives have been defined in the present work. The first objective is to show that the cononsolvent route can be used to successfully form asymmetric hybrid membranes and to study the impact of the PEI concentration and of the composition of the nonsolvent liquid mixture on the membrane porous structures. The second objective is to *in situ* grow the Pd nanoparticles in the asymmetric hybrid membranes for a large range of Pd content. The efficiency of two different *in situ* generation routes and their consequences on the Pd nanoparticle location are discussed. The third objective is to determine the gas transport properties of the asymmetric nanocomposite membranes and to discuss their hydrogen separation properties.

2. Experimental

2.1. Materials and precursor hybrid film preparation

Polyetherimide (PEI, Ultem 1000, $26,000 \text{ g mol}^{-1}$) was obtained from Sabic. Palladium acetate ($PdAc_2$, purity higher than 99%) was purchased from Fluka. N-methyl pyrrolidone (NMP, grade for analysis), methylene chloride (MC, grade for analysis) and acetone were purchased from Acros Organics.

PEI was dried under vacuum at 110°C for 7 h prior to be used. Metal doped polyetherimide solutions containing from 10 to 20 wt% of polymer were prepared from PEI, MC and $PdAc_2$. The metal complex content was varied in order to cover a wide range of Pd amount in the final film, e.g. from 0 to 15 wt%.

The solutions were cast in an open mould and then immediately immersed for 5 min into a bath containing a NMP/MC solution of defined composition. The casting solutions which became opaque due to the formation of the porous structure were immersed into an acetone bath for 8 h to remove the residual solvent. The precursor porous films were finally dried at room temperature.

2.2. Nanostructuring routes

The free standing precursor membranes were treated according to two routes to *in situ* grow the metal nanoparticles. The same treatments were performed on neat PEI membranes to prepare reference membranes.

The first route consisted in a thermal treatment. The annealing conditions were chosen from a preliminary work [29] as the most efficient ones to generate the metal nanoparticles while keeping defect free membranes with low residual solvent content: The thermal treatment consisted in a temperature ramp from 20°C to 220°C at a rate of $6^\circ\text{C}/\text{min}$ followed by an additional annealing time of 1 h at 220°C . These treatments were performed in all cases under air atmosphere. The samples were taken off from the oven after the treatment and placed in a conditioned room (22°C , 30%RH) to ensure a similar cooling process. The nanocomposite films obtained from annealing were referred as *a-Xwt%Pd*, where X represents the final Pd to PEI ratio expressed in weight percent (assuming a total conversion of $PdAc_2$ into metallic Pd).

The second route consisted in a chemical reduction performed by immersion of the precursor membranes in a freshly prepared methanol–sodium borohydride ($NaBH_4$) solution just after swelling the membrane in methanol. Methanol (MeOH, 99.8%) and sodium borohydride ($NaBH_4$, >98%) were purchased from Acros Organics. We worked with a $NaBH_4$ excess: the molar $NaBH_4$ to metal complex ratio was fixed to 4 [29]. After an immersion time

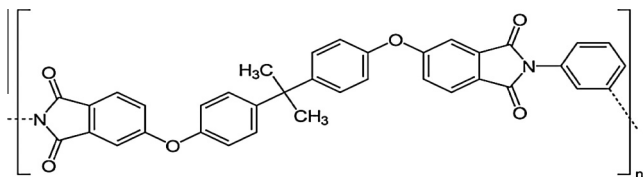


Fig. 1. Chemical structure of polyetherimide.

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