

Evaluation of electrospun nanofibrous mats as materials for CO₂ capture: A feasibility study on functionalized poly(acrylonitrile) (PAN)



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ARTICLE INFO

Keywords:

Electrospinning
Nanofiber mat
CO₂ capture
Gas separation
Facilitated transport

ABSTRACT

We fabricated a new type of nanostructured materials for CO₂ capture processes, based on poly (acrylonitrile), PAN, a polymer almost impermeable to CO₂, but easily functionalizable and spinnable. The preparation involved amine functionalization of PAN powder, electrospinning of the powder to form a nanofibrous mat with a large surface area, and compression of the mat to obtain dense membranes for facilitated transport of humid CO₂. The functionalization step was carried out with different routes: amination with hexamethylene diamine or ethylene diamine, and basic hydrolysis. The final amine content in the polymer could be tuned varying the reaction type and conditions, although high functionalization degrees led to crosslinking, which made the powder insoluble.

The dry CO₂ uptake was measured at various stages of the preparation, in order to assess separately the effect of chemical functionalization and surface area enhancement on the material capture ability. Such tests indicated that both chemical and morphological changes of the neat polymer enhanced the dry CO₂ sorption capacity, although the increase of surface area yielded the largest improvement.

CO₂ permeation tests in humid conditions were carried out on the compacted membranes, indicating that the materials functionalized via direct amination exhibit a behavior compatible with the facilitated transport mechanism, with CO₂ permeability reaching 83 Barrer, increasing by 17 times with respect to the dry state value, at a relative humidity of 50%. Membranes functionalized via hydrolysis did not show such a behavior, maybe because the amine functionalities were consumed by an unwanted reaction. The procedure can be further improved by optimizing each processing step, or changing the order of the steps. The electrospinning process seemed the key factor of the approach, as the large surface area of electrospun mats allowed to obtain membranes with a higher permeability than the original ones, and a large availability of amine groups useful for humid CO₂ capture.

1. Introduction

The separation of CO₂ from gaseous mixtures is gaining attention because, besides the industrial separation needs, such as natural gas sweetening, syngas purification and biogas upgrading, this process could help to reduce CO₂ emissions in the atmosphere [1–6].

Membrane-based separations can compete with conventional CO₂ capture and removal processes [4,5,7–9], like chemical absorption, although they still present some disadvantages. The most important one is that an increase of membrane selectivity is usually accompanied by a decrease in permeability, with a consequent reduction of process productivity [10].

A scarcely known but important aspect is the effect of humidity on the membrane performance. The presence of humidity can reduce the membrane gas permeability, up to 70% in certain polyimides like

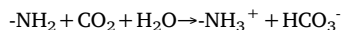
Matrimid® and 6FDA-6FpDA [11,12], which are suitable for gas separation due to high selectivity, mechanical and chemical stability [13,14]. On the other hand, humidity favors the gas permeation in certain hydrophilic polymers like Nafion® [15], and its presence in the gas feed is essential for the separation performance of the so-called “facilitated transport” (FT) membranes.

Facilitated transport of oxygen with hemoglobin carriers was first shown by Scholander [16], and attracted the attention of membrane developers since then. Indeed, fixed and mobile carriers opportunely placed in a membrane can selectively enhance the permeation of a target gas, like CO₂, that undergoes a reversible reaction in the presence of water and carriers. All the other gases, like N₂, can permeate only by solution-diffusion mechanism. Suitable carriers for facilitated transport of CO₂ are for instance amines, which can be easily attached covalently to a polymer matrix (fixed carriers). The presence of water allows the

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reaction involving CO₂ and the carrier [17–19]:



It is proven that HCO₃[−] ions form within the membrane and diffuse across it, then reconvert to CO₂ on the downstream side, releasing the OH[−] group and making it available for the following CO₂ molecule [17–26]. Such reaction proved to boost the selectivity towards CO₂ of the membrane.

Several researchers reported that fixed site carrier membranes show enhanced stability with respect to mobile carrier membranes. For instance, fixed amine carriers were incorporated by Huang et al. [18] in polyvinylalcohol (PVA) and used to increase CO₂/N₂ selectivity up to 170 °C. Deng et al. [19] fabricated polyvinyl alcohol (PVA) and polyvinyl amine (PVAm) blends, obtaining CO₂/N₂ separation factor around 174 and CO₂ permeance up to 0.58 m³(STP)/m^{−2} h^{−1} bar^{−1}.

The studies investigating the facilitated transport of CO₂ usually quantify the facilitation factor, defined as the ratio between the gas flux with facilitation to the one without facilitation. This factor depends on operative conditions, like temperature and pressure, and may also vary with membrane thickness [27,28].

Many polymers have been, or can be functionalized with amine groups to produce fixed carrier membranes. One of them is Polyacrylonitrile (PAN), that is a commercially important polymer with many desirable properties like solvent and abrasion resistance, thermal and mechanical stability, high tensile strength [29–31].

Active nitrile groups present in PAN allow for the introduction of new functional groups (e.g. amine ones) by specific reactions [29,32,33]. Up to now, aminated PAN electrospun membranes have been used as supports for organic compounds, enzymes and antibodies in biological studies as well as catalysts [31,33]. They have also been used for immobilization of various organic ligands for adsorption of metal ions in water. Furthermore, because of their ability to complex metal ions, several surface-modified PAN electrospun nanofibers have been used as supports for transition metal catalysts in Fenton's chemistry [30].

In this work we focused the attention on the experimental fabrication and preliminary characterization of amine-functionalized PAN materials for CO₂ capture. The target is to obtain nanofibrous mats by electrospinning of functionalized PAN, which can be used directly as adsorbent materials, or further processed to compact the structure and obtain a dense membrane to be used in gas permeation systems with a facilitated transport mechanism.

To the best of our knowledge, no study in the literature ever evaluated materials based on electrospun nanofibrous polymeric mats, either functionalized or not, as selective devices for gas separation and/or for CO₂ capture processes.

Some previous works were devoted to the study of CO₂ adsorption onto commercial micrometric fibers of PAN and other polymers functionalized with different techniques [34,35]. In other cases, the procedure, similar to the one inspected here, that involves an electrospinning step followed by a compaction of the polymeric mat to obtain a membrane was applied to a different field, namely the production of membranes for fuel cells [36].

The first step to obtain such materials was the functionalization of the PAN powder with amine groups: different routes were analyzed and tested to this aim. In particular, we considered the reaction of direct amination in the presence of hexamethylene diamine (HMDA) or ethylene diamine (EDA) and basic hydrolysis. The reaction times, temperatures, and reactant compositions were varied in a wide range in order to find the conditions that guarantee an optimal functionalization degree. The maximization of the number of amine groups attached was pursued without losing the processability of the material. Indeed, it is known from literature that when a polymer is functionalized with amine groups, crosslinks can form between the chains [13]. The crosslinking reaction had to be carefully avoided in our case, as the

polymer became insoluble in the solvent chosen for the subsequent electrospinning process.

The electrospinning technique was then applied to the functionalized polymer, in view of maximizing the surface area and the availability of amine groups for separation of gas mixtures in adsorption or membrane processes. Indeed, functionalized nanofibrous mats could, in principle, be used as adsorbents due to their high surface area, and large availability of functional groups with a chemical affinity for CO₂.

Subsequently, the functionalized mats were compacted via compression moulding to produce dense membranes suitable for CO₂ separation. The aim was to evaluate if these compacted structures can still offer active amine groups able to favor, in a humid environment, a facilitated transport mechanism for CO₂. If verified, such approach can offer an alternative method to produce fixed site carrier FT membranes.

We tested the behavior of the materials at different stages of the preparation protocol, to assess separately the effect of chemical and physical modifications to the capture properties of the materials. In particular, we measured dry CO₂ uptake in the initial PAN powder and in the different functionalized powders, to study the effect of chemical functionalization and establish a correlation between the CO₂ uptake and the amount of amines present. Then, we quantified the same property in electrospun mats and in compacted membranes obtained from them, to correlate the CO₂ sorption ability to the morphology of the system. Finally, we carried out CO₂ permeation tests on the compacted membranes at different relative humidities, in order to verify the occurrence of a facilitated transport mechanism.

2. Experimental

2.1. Materials

Polyacrylonitrile (*M_w* = 150,000 g/mol), hexamethylene diamine, sodium hydroxide and N,N-dimethylformamide (DMF, used as a solvent after dehydration by storage over molecular sieves) were purchased from Sigma-Aldrich, USA. Ethylene diamine was kindly supplied by Xenochimica (Italy).

2.2. PAN powder functionalization

Polyacrylonitrile in powder was functionalized following two different routes, using reaction with aqueous solution of different diamines (HMDA or EDA) or by hydrolysis in a basic aqueous solution (NaOH 1 M) according to the reaction schemes in Fig. 1 [29,33]. As it can be seen in Fig. 1b, such latter reaction can also lead to the unwanted formation of carboxylate groups, which removes the amine functional groups from the polymeric matrix.

It is known that primary and secondary amines interact directly with CO₂ [37], therefore in this work we chose two primary diamines of different size (EDA, HMDA), in order to understand the effect of chain length on the properties of functionalized PAN.

The reaction of functionalization with both HMDA and EDA amines (Fig. 1a) was conducted in a three neck flask, equipped with a reflux condenser, contained in a thermostatic oil bath. It was reported that the reaction conversion is strongly affected by the reaction time and temperature as well as amine concentration [38]. In order to study the effect of process conditions on polymer functionalization and spinnability, amine-distilled water solutions and PAN were loaded in the reaction environment with amine excess ranging mainly from 2 to 10 times the stoichiometric ratio, although we investigated values as high as 100. The reaction temperature was varied between 80 and 110 °C, the reaction time between 1 and 6 h. We selected also higher reaction temperatures than those reported in literature for a similar synthesis [39], in order to maximize the degree of polymer amination. During the functionalization reaction, the polymer powder changed color from white to orange, depending on the conversion degree reached. The reacted polymer powder was washed with distilled water until

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