



Hydrogen purification for PEM fuel cells using membranes prepared by ion-exchange of Na-LTA/carbon membranes

Francisco J. Varela-Gandía, Angel Berenguer-Murcia, Dolores Lozano-Castelló, Diego Cazorla-Amorós*

Departamento de Química Inorgánica, Universidad de Alicante, Ctra. San Vicente del Raspeig s/n, Ap. 99, E-03080 Alicante, Spain

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ABSTRACT

Modified LTA membranes supported on macroporous carbon discs have been synthesized for the separation of H₂ and CO. These membranes have been prepared by hydrothermal synthesis following the secondary growth method and subsequently ion-exchanged with different alkaline cations in order to modify the zeolite pore size. Their permeation properties have been studied for the purification of a hydrogen stream (50 vol.%) containing carbon monoxide (1.25 vol.%). For this purpose, a Wicke–Kallenbach cell has been used to perform the separation experiments. Single gas permeation properties and bicomponent mixtures were carried out at three different temperatures (298 K, 398 K and 423 K). Our results indicate that even the K-LTA form would be suitable for the purification of H₂ at room temperature. The Rb- and Cs-forms exhibit the best performance, in which CO permeation is blocked at all temperatures studied. As a result, a high purity H₂ stream may be obtained by employing the Rb- and Cs-membranes derived from Na-LTA/carbon membranes.

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1. Introduction

In the near future, hydrogen economy is expected to be implemented due to the necessity of a clean, efficient energy source and the growing energy crisis [1]. Hydrogen has several advantages as a fuel compared to conventional fossil fuels. Its combustion does not produce pollutants such as carbon dioxide, nitrogen oxides, particles or carbon monoxide and thus presents itself as an interesting alternative. It can be used for mobile and stationary devices mainly in transport vehicles. Nevertheless, one of the most significant shortcomings is the storage of the produced hydrogen, so a more convenient source is needed as a transient solution in order to use it in polymer electrolyte membrane (PEM) fuel cells. The main advantage of PEMs is their being twice as fuel efficient as an internal combustion engine. They operate transforming chemical energy into electrochemical energy, avoiding the mechanical requirements and thermodynamic limitations of conventional engines [2]. Hydrogen and oxygen react electrochemically and water is produced as remainder so it is a clean process.

Ideally, hydrogen may be obtained from renewable sources like water by electrolysis but this technology is not sufficiently developed. Nowadays, hydrocarbon reforming is the most prominent industrial process to produce hydrogen. Vehicles may carry an on-board reformer which would produce a hydrogen stream from the reforming of hydrocarbons like ethanol or methanol. However, in

the hydrogen produced there are some compounds that poison the platinum sulphur catalyst in the anode, more specifically sulphur and carbon monoxide. Thus, concentrations lower than 10 ppb and 10 ppm, respectively are needed to avoid poisoning. After the reforming step and water gas-shift reaction, the sulphur concentration is reduced to desirable levels but another step is needed to reduce the CO concentration from 0.1 to 1% (the concentration of the gaseous stream leaving the reformer) to values around 10 ppm [2].

One alternative to purify hydrogen is the use of hydrogen selective membranes due to their easy preparation, low energy consumption and cost effectiveness at low gas volumes [3]. There are several kinds of membranes which can be organized into three categories: (i) polymeric, (ii) metallic and (iii) inorganic membranes like zeolite membranes. Polymer membranes have several advantages like having a low cost and not causing significant pressure drops. However, mechanical strength problems and high sensitivity to swelling and compacting reduce their usefulness for this purpose [4]. The second type, metallic membranes, have an excellent hydrogen permeance but suffer from hydrogen embrittlement at low temperatures [5]. This is eliminated by using alloys but the product is more expensive. The latter, zeolite membranes, combine the general advantages of inorganic membranes like temperature stability and solvent resistance with those of polymeric membranes as they are composed of a thin homogeneous layer.

In the literature, there are many reports on zeolite membranes but the studies have been focused from a different point of view. Caro and Noack [6] have presented a review about zeolite membranes which are focused on separating gases like CO₂ or CH₄ from

* Corresponding author. Tel.: +34 965903946; fax: +34 965903454.
E-mail address: cazorla@ua.es (D. Cazorla-Amorós).

H₂. Noble and co-workers [7] have studied hydrogen purification using a SAPO-34 membrane with the aim to remove CO₂ and CH₄. However, the separation of H₂/CO mixtures has been solved by means of other methods. In this case, the use of palladium and reactive membranes has been studied [8,9]. In first place, Drioli and co-workers [8] described the effect produced by CO concentration in the H₂ permeation properties at different temperatures towards the design of a hydrogen purification unit. Secondly [9], they have studied Pt–Y zeolite tubular membranes prepared by the secondary growth method. This reactive membrane is used for the preferential oxidation of CO, reducing its concentration from 10,000 ppm to 10–50 ppm. However, the use of zeolite membranes in the separation of H₂/CO mixtures is a new, although extremely important matter, which has not been studied in detail yet.

In correlation to zeolite membrane performance, the single gas permeation properties of different gases have been widely studied. Nitrogen, which has a similar kinetic diameter to carbon monoxide, has been extensively studied in several papers [10,11]. Aoki and co-workers [12] studied the single gas permeation properties of a LTA membrane on a porous α -alumina substrate obtaining a better permeance for hydrogen than for nitrogen. Finally, Kusakabe and co-workers [13] have studied the permeance of different gases in ion-exchanged LTA zeolite membranes.

LTA zeolite (also known as zeolite A) is formed by sodalite cages (β) connected through double four member rings (MR) which form a larger cavity denominated α supercage. The former cage presents 6MR openings of 0.2 nm in size and the inner cavity that is formed has a diameter of 0.66 nm. The latter cage is connected by 8MR openings of 0.41 nm in size and the inner cavity formed has a diameter of 1.12 nm [14].

The original pore size (0.41 nm) may be fine-tuned by means of substituting the cations incorporated in the structure (and which bring forth charge balance) by a simple ion-exchange process. According to Breck and co-workers [14], the LTA zeolite can be ion-exchanged with different cations, such as alkaline ions. Depending on the cation, the pore size may be changed. Initially the synthesized zeolite has sodium as counterion (because Na⁺ also acts as templating agent for LTA zeolite) which produces an effective pore size of 0.38 nm. When this zeolite is ion-exchanged with potassium, the effective pore size is reduced to 0.28 nm. Nevertheless, a partial ion-exchange with a calcium salt produces a larger pore size of 0.51 nm. Bearing in mind the modification of the pore size, if the Na-form is ion-exchanged with either Rb or Cs (which are substantially larger cations), the expected pore size would be lower than that of the K-form. Therefore, by changing the cations, the zeolite A can be used for different purposes.

This work reports the synthesis of Na-LTA membranes supported on a carbon material by hydrothermal treatment following the secondary growth method, as well as K-, Rb- and Cs-LTA/carbon membranes prepared by means of ion-exchange. Carbon discs were used as support due to their outstanding properties, such as thermal and chemical stability, tunable shape, porosity and surface chemistry that provide advantages comparing it with metal and ceramic supports [15]. The gas permeation properties of the prepared composites were tested using small molecules (H₂ and CO) at different temperatures with the objective to understand their usefulness for hydrogen purification for PEM fuel cells.

2. Experimental

2.1. LTA/carbon membrane preparation

LTA/carbon membranes were prepared by the secondary growth following the methodology described in our previous works [15]. Initially, the carbon support, consisting of macroporous carbon

sheets (thickness = 0.3 mm, mean pore size 0.7 μ m, geometric area 1.54 cm²) provided by Poco Graphite (DFP-1), was cut into pieces and subjected to an acid treatment which consists in immersing the carbon pieces in boiling concentrated nitric acid for 12 h in order to create surface oxygen groups. Secondly, the treated carbon support was seeded by means of electrophoretic deposition (EPD) using a LTA colloidal suspension for 30 min. The employed seeds were prepared by hydrothermal treatment using a synthesis solution with the following molar composition: 0.22Na₂O·SiO₂·1.0Al₂O₃·8.0(TMA)₂O·400H₂O. The hydrothermal conditions were a synthesis temperature of 336 K for 63 h. Finally, a hydrothermal synthesis was carried out over the seeded support and a thin zeolite film was grown. The molar composition of this LTA synthesis solution was 50Na₂O·5.0SiO₂·1.0Al₂O₃·1000H₂O and the hydrothermal conditions were a synthesis temperature of 373 K for 4.5 h.

The prepared Na-LTA/carbon membranes were ion-exchanged according to the method described by Rakoczy and Traa [16]. The membrane was immersed into a 0.1 M alkaline ion nitrate solution and heated at 333 K for 1 h under mild agitation (60 rpm) to prevent damage to the zeolite layer.

It is important to note that Na-LTA powder zeolite has been synthesized and ion-exchanged in the same manner, due to the fact that it is impossible to use the zeolite on the membrane support to characterize its adsorption properties.

2.2. Membrane characterization

Firstly, LTA/carbon membranes and LTA zeolite powder (obtained from the same autoclave) were characterized by X-ray diffraction (XRD), using a SEIFERT 2002 power diffractometer with a Cu K α radiation. The scanning rate was 2°/min in the 5–50° angle range.

The LTA/carbon membranes were also characterized by scanning electron microscopy (SEM) in a HITACHI S-3000N microscope and the morphology and thickness of the thin film prepared was studied. Energy-dispersive X-ray spectrometry (EDX) was used to ascertain if the ion-exchange method had been carried out successfully. Incident electron beam energies from 3 keV to 30 keV were used.

Finally, the recovered powders of the synthesized zeolites were used to study H₂ and CO adsorption at 298 K and up to ambient pressure (Micromeritics ASAP2020) with the aim to assess their adsorptive properties. Moreover, porous texture characterization of these zeolites was carried out by means of the adsorption of N₂ at 77 K (Micromeritics ASAP2020) and CO₂ at 273 K (Autosorb 6, Quantachrome). Prior to the adsorption measurements, the samples were outgassed in vacuum at 523 K for 4 h to remove any adsorbed impurities.

The permeation measurements were performed in a Wicke–Kallenbach (WK) cell. The membrane was mounted in a stainless steel module and sealed by means of polymeric O-rings to prevent leaks. The final exposed area in the WK was 0.28 cm². Firstly, the membrane was cleaned by heating it at 423 K for 6 h under a He flow of 100 ml/min on both the feed side and the permeate side with the aim of removing impurities. The permeation tests were carried out between 298 K and 423 K, with a total pressure of 1 bar. In the single gas permeation tests, the feed gases used were diluted in He (50% H₂ or 1.25% CO). In the H₂/CO mixture permeation tests, the binary mixture was diluted in He with a composition of 50% H₂ and 1.25% CO. For both types of experiments, the total flow rate was 100 ml/min. A sweep gas (He, flow rate of 100 ml/min) was used in order to remove the gas/gases that flow through the membrane, hence the system is always in pseudo-equilibrium. The permeate stream was analyzed with a mass spectrometer (Balzer, Thermostar GSD 301T). The

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