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Effect of process parameters on electroless plating and nickel-ceramic composite membrane characteristics

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ABSTRACT

In this article we address the process perspective of electroless plating technique to fabricate nickel-ceramic composite membranes. In this work, we also report an inexpensive ceramic membrane precursor formulation which upon sintering process yielded a membrane support with an average pore size of 275 nm. Subsequently, membranes were subjected to electroless plating for wide choice of nickel solution concentration (0.04–0.16 mol/L) and loading ratio (defined as membrane area per unit plating solution volume) values (196–393 cm^2/L). Various parameters evaluated to relate upon plating and membrane characteristics are conversion, plating efficiency and inefficiency, metal layer thickness and average nickel-ceramic membrane pore size. In general it was observed that sodium hypophosphite based electroless nickel baths provided lower conversion (10–40%) and moderately higher efficiencies (90–60%). However, the effect of loading ratio on efficiency was found to be insignificant. On the other hand, membrane densification was observed to vary between 78–90% to yield a surface pore size reduction from 275 nm to 128–90 nm. Retail cost based analysis further indicates the non-linear dependencies of both chemicals cost and metal layer thickness with respect to the percent pore densification values.

1. Introduction

Numerous applications exist for inorganic membranes due to their adaptability at higher temperatures. These include hydrogen purification, fuel cell technology and membrane reactor processes. So far, emphasis in this fascinating area of research has been largely towards palladium and palladium-alloy composite membranes [1–5]. Amongst various techniques available for metal-ceramic composite membranes, electroless plating is the most prominent due to several advantages such as ease of preparation, scale up, uniform deposition, ability to deposit on complex shapes. Recent experimental trends in metal-ceramic membrane technology indicate upon a surge towards nickel-ceramic composite membranes [6–9]. This is mainly due to two reasons. Firstly, palladium being expensive increases the cost of the metal-ceramic membrane significantly. Secondly, palladium membranes are susceptible for embrittlement during temperature cycling.

Ernst et al. [9] prepared nickel-ceramic composite membranes using a support that is deposited with γ-Al_2O_3 skin layer. The authors did not elaborate upon the plating process conditions and only deposited a porous metallic nickel layer of about 1–1.5 microns on the support surface. While reasonable separation factors (28 for H_2/N_2 in the presence of a sweep gas) were obtained, the membrane fluxes were fairly low. Therefore, the long term applicability of nickel membranes for gas separation needs to achieve higher trans-membrane fluxes and separation factors and these values shall be comparable with the values obtained for dense and porous palladium composite membranes.

In few articles, electroless plating chemistry and pertinent reaction kinetics have been thoroughly investigated [1,10]. Certain studies indicate that hydrazine hydrate as a reducing agent serves better than sodium hypophosphite [11]. This is probably due to the release of N_2 in the former case than H_2 (which is released in the later case) which does not strongly induce shear effects on the membrane surface. However, hypophosphite baths cannot be ignored since hydrazine is a class-II carcinogen. Further, several other studies indicate that the availability of a skin layer with reduced pore size contributes significantly to reduce the metal film to achieve a dense metal-ceramic membrane [12–14]. More recently, mass transfer effects have been identified to play a dominant role in enhancing membrane densification and permeation characteristics [15,16].

The wider applicability of metal-ceramic membranes is significantly dependent on issues related to the scale up and process design of the electroless plating technique. While dense membrane fabrication is mandatory using electroless plating technique, adopting best possible combinations of electroless plating parameters is also essential to reduce the total cost of chemicals expended for the membrane fabrication. The cost related issues are more significant for noble metal deposition, as the cost of the noble metals is significantly higher than other metals. Amongst several process parameters, loading ratio (membrane area per unit volume of plating solution) and solution concentration of the metal

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are the most relevant. These parameters greatly influence process efficiency which can be conveniently defined as the amount of metal deposited on the unit membrane surface. It is evident that due to the pertinent release of N_2/H_2 gas from membrane surface, shear effects induce the removal of loosely deposited metal on the membrane surface. Eventually, the isolated metal in the plating solution contributes to an undesirable additional metal deposition acting as seeding catalyst. Thereby, the efficiency of the electroless plating is significantly reduced. Therefore, both solution concentration and loading ratio involve tradeoffs. Low loading ratio values provide higher process efficiencies. However, larger number of plating sequential steps is required to prepare a membrane with desired permeation characteristics. In other words, low loading ratio values contribute to higher costs of membrane fabrication process. However, higher loading ratio values provide lower process efficiencies and membranes with desired characteristics can be prepared with lower number of plating sequential steps. Henceforth, an optimal loading value shall yield metal-ceramic membranes with an optimal combination of process efficiency and number of sequential plating steps and hence cost. A similar trend in tradeoffs with respect to solution concentration can be visualized. Since electroless plating is an autocatalytic reaction, the time dependent quantity of metal deposited on the surface significantly influences reaction kinetics. Therefore, lower concentration of metal in the plating solution leads to lower surface concentration of nickel and hence lower reaction rates, H_2/N_2 generation, associated shear effects and higher process efficiencies (and good morphologies). However, densification of the membrane under these circumstances requires more number of sequential plating steps and hence higher costs. On the other hand, higher concentration of metal in the plating solution involves higher metal deposition rates, H_2/N_2 generation and associated shear effects and lower process efficiencies and poor metal-ceramic morphologies. Eventually, densification of the membrane also requires larger number of sequential plating steps. Henceforth, an optimal concentration shall provide optimal combination of reaction rate, membrane surface densification and number of plating sequential steps and hence cost of fabrication.

Some studies in metal-composite membrane preparation using electroless plating involved a metal solution concentration of 0.0033 mol/L (for both Pd and Ag precursors) and loading ratio of 60 cm^2/L [4]. However, when higher Pd metal precursor concentrations (about 0.0307 mol/L) were used [17] the loading ratio was increased to 785 cm^2/L. In other words, it appears that loading ratio is proportionally adjusted to the metal concentration without much technical justification. In summary, the combinatorial effect of loading ratio and metal solution concentration on process efficiency, membrane thickness and densification has not been reported.

Emphasizing upon the need to utilize inexpensive ceramic supports so as to reduce the overall cost of the composite membrane, this work addresses parametric studies to evaluate the combinatorial effect of loading ratio and metal solution concentration on conversion, process efficiency and membrane densification. The efficacy of sodium hypophosphite as a reducing agent for membrane densification was targeted in this work. Since nickel plating is inexpensive when compared with the palladium electroless plating, nickel was chosen to generate data that can be also referred in future experimental investigations. The nickel solution concentration was varied between 0.04–0.16 mol/L. Corresponding variation in loading ratio was about 196–393 cm^2/L. A maximum plating time of 8 h involving 8 sequential 1 h plating steps was taken as the basis to streamline the experimental investigations for the comparative assessment. The primary objective of this work is to investigate electroless plating process parameters using an inexpensive material such as nickel that can mimic the electroless plating performance characteristics of palladium composite membranes. On the other hand, it is also anticipated that this work serves as a general guideline towards the fabrication of nickel-composite membranes for definitive application in gas separation in the near future.

2. Experimental

2.1. Support preparation and characterization

Seven inorganic raw materials viz. kaolin, feldspar, quartz, sodium carbonate, pyrophyllite, boric acid and sodium metasilicate were used in the fabrication of ceramic membrane supports. Kaolin was obtained from CDH Ltd., India, feldspar and pyrophyllite from National Chemicals, India, quartz from Research-lab Fine Chem Industries, India, sodium metasilicate from SD Fine-chem Ltd., India and the other inorganic precursors (sodium carbonate and boric acid) were obtained from Merck Ltd., India. Composition of various raw materials mentioned above is shown in Table 1.

The fabrication methodology consists of the following hierarchical steps: mixing of raw materials to make a paste; casting of the paste into circular moulds; drying of the raw discs; sintering; polishing of the membranes and cleaning. All the raw materials except water were taken based on the above composition with a total dry weight of 20 g for one membrane. These raw materials were manually mixed and ground to make a uniform powder and then mixed thoroughly using a laboratory blender. This dry mixture was taken into a container and water was added to it (approx. 5 ml for each membrane) and manually mixed to form a uniform paste. The paste was then placed into a circular mould (stainless steel) to make disc shaped membranes. Weights were placed on the wet membranes for about 12 h to recover structural deformations and then the membranes were dried for 24 h at ambient conditions (298 K). After ambient drying, they were kept in a muffle furnace for another 12 h at 373 K to remove the moisture content of the membranes. The membranes were then sintered. The temperature of the furnace was increased up to the sintering temperature (1173 K) in two steps. Initially, heating was carried out at a slower rate (1 K/min) up to 523 K to avoid bending/cracking of membranes followed by a slightly higher heating rate (2 K/min) up to the sintering temperature. Sintering was carried out for four hours and the membranes were allowed to cool down to the room temperature. The sintered membranes were polished using silicon carbide abrasive paper (no. 220) to obtain a smooth surface finishing with required dimensions (52.5 mm diameter and 4.5 mm thickness) and were cleaned in an ultrasonic bath using de-ionized water.

Membrane characterization was studied using various preliminary methods [18]. The surface characterization was done by scanning electron microscopy (SEM). The mean pore size of the bulk membrane was estimated from air and water permeation experiments. Membrane porosity was obtained by pycnometric method. Membranes were also tested for their corrosion resistance using standard HCl and NaOH solutions for a period of 7 days. A weight loss of less than 5% was observed for the membranes which was kept in the acid bath (pH = 1) and no weight loss was observed for the membrane kept in the basic bath (pH = 13) inferring that they are suitable for the plating conditions.

Table 1
Composition of raw materials for the fabrication of ceramic membrane supports.

Material	Composition on dry basis (wt.%)	Composition on wet basis (wt.%)
Kaolin	40	32
Feldspar	15	12
Quartz	15	12
Na_2CO_3	10	8
Pyrophyllite	10	8
Boric Acid	5	4
Sodium metasilicate	5	4
Water	–	20