Journal of Membrane Science 540 (2017) 243–250

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Highly gas permeable, ultrathin Teflon AF2400/γ-alumina composite hollow fiber membranes for dissolved gas analysis

Sainan Liu[a], Liang-Chih Ma[a], Chien-Hua Chen[a,b], Chuan Chen[c], Y.S. Lin[a,*]

[a] School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287, USA
[b] Department of Chemical Engineering, National Taiwan University, Taiwan ROC
[c] Global Energy Interconnection Research Institute, PR China

ARTICLE INFO

Keywords:
Teflon AF2400
Ultrathin membrane
γ-alumina
Hollow fiber
Dissolved gas analysis

ABSTRACT

Dissolved gas analysis (DGA) is a useful approach to monitor the electrical faults of transformers. For extraction of dissolved gases from transformer oil in the DGA process, membrane-based separation represents an appealing technology option since the use of an oil-resistant, stable and highly gas permeable dense membrane can greatly enhance the efficiency by shortening the extraction time. However, most membranes reported in the literature have a membrane thickness in the micrometer range, making these membrane devices not sufficiently effective in practical separation of dissolved gasses from transformer oil. To reduce the thickness of membranes, Teflon AF2400 composite membranes synthesized using three different types of alumina (Al_2O_3) supports were investigated, including macroporous α-Al_2O_3 disk support, macroporous α-Al_2O_3 hollow fiber support, and mesoporous γ-Al_2O_3/α-Al_2O_3 hollow fiber support. The result shows that the γ-Al_2O_3/α-Al_2O_3 supports with a mesoporous top-coating γ-Al_2O_3 layer prepared by the sol-gel method could provide a high-quality surface for synthesizing an ultrathin and defect-free Teflon AF2400 layer. For the ultrathin Teflon AF2400/γ-Al_2O_3 composite hollow fiber membranes prepared by coating with a 0.5 wt% Teflon AF2400 solution, the thickness of the Teflon AF2400 layer is about 270 nm, and the permeances of H_2, CH_4, CO_2 and C_2H_6 at room temperature can reach to 14,069, 2847, 11,901 and 2030 GPU, respectively, which are about 8 times higher than that of the α-Al_2O_3 disk or hollow fiber supported membranes. This result demonstrates the promise of the ultrathin Teflon AF2400/γ-Al_2O_3 composite hollow fiber membranes for extraction of dissolved gases from the transformer oil for DGA.

1. Introduction

Liquid-immersed transformer is a critical component of the electrical grid for increasing and decreasing the alternating voltages in electric power applications. In practice, transformers are filled with insulating oil that surrounds the transformer coils. Typically, the insulating oil is based on mineral oil, and the composition should be around C-17 to C-40 carbon chains' alkanes. Electrical insulation paper (or called transformer board) as an insulating material is also required for withstanding the high electrical and physical stresses experienced around a core and windings in liquid-immersed transformers. When an abnormal phenomenon occurs (such as arcing, partial discharge, or overheating), the insulating oil and paper may decompose and generate gases consisting of H_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, and C_2H_6 which can be dissolved in the oil. The composition of liberated gases can reflect the type of electrical fault [1], and thus, the dissolved gas analysis (DGA) is considered as a useful approach for the preventative maintenance program.

Extraction of dissolved gases from transformer oil is a key step in the DGA process, which is conventionally achieved by the vacuum or headspace method [2]. In this method, the gases can be extracted from the oil and then collected through evacuating, agitating and heating the oil due to the change of the equilibrium position. Membrane-based separation represents a new and appealing technology option for extraction of dissolved gases from transformer oil. Compared with the traditional vacuum method, membrane-based separation displays higher efficiency for dissolved gas extraction since it offers continuous operation and is essentially free of maintenance. The success of this separation process depends on the development of a dense polymeric membrane that allows only gases to freely pass through and provides a barrier to oil.

For the selection of membrane materials, good chemical and thermal stability as well as high gas permeability are required. Several polymers have been studied, including tetrafluoroethylene-

* Corresponding author.
E-mail address: Jerry.Lin@asu.edu (Y.S. Lin).

http://dx.doi.org/10.1016/j.memsci.2017.06.064
Received 27 April 2017; Received in revised form 23 June 2017; Accepted 24 June 2017
Available online 27 June 2017
0376-7388/

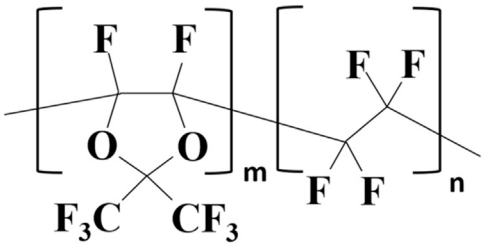

Fig. 1. Chemical structure of Teflon AF2400.

perfluoroalkylvinylether (PFA) [1], polyimide (PI) [3], polytetrafluoroethylene (PTFE) [4], fluorinated ethylene propylene (FEP) [5] and Teflon AF2400 [6]. Most of them are fluoropolymers (namely PFA, PTFE, FEP and Teflon AF2400). PTFE is a homopolymer derived from polymerization of tetra-fluoroethylene (TFE), while the others (PFA, FEP and Teflon AF2400) are block copolymers with a composition of a subunit of TFE and another different subunit. Among these polymers, Teflon AF2400, an amorphous glassy copolymer of TFE and 2,2-bis-trifluoromethyl-4,5-difluoro-1,3-dioxole (BDD) [7], is recognized as a promising membrane material for oil-gas separation in terms of gas permeability, oleophobicity, and thermal and chemical resistance. The chemical structure of Teflon AF2400 is shown in Fig. 1. It has high fractional free volume because of the rigid structure of dioxolane ring and smaller van der Waals interactions between chains, leading to excellent gas permeability [8]. Furthermore, owing to the high stability of carbon-fluorine bonds, Teflon AF2400 possesses similar thermal and chemical resistance properties of PTFE [9].

As reported in the literature [1,3–5], the membranes prepared for oil-gas separation had a thickness in the range from 12.5 to 180 μm. Even though they showed good chemical and thermal stability in the separation process, the gas permeance did not meet the requirement for high efficiency due to the membrane thickness. To improve the permeance by reducing the membrane thickness, Han et al. [6] prepared the Teflon AF 2400/ceramic composite membrane by depositing a thin Teflon AF2400 layer with a thickness of 8 μm on the porous ceramic tube, which enhance the oil-gas separation efficiency. It should be pointed out that porous ceramic materials have advantages of excellent chemical, mechanical and thermal stabilities, which are usually used as the substrate for synthesizing a composite membrane. Jin and co-workers developed a series of organic/ceramic composite membranes for liquid-gas separation. These composite membranes exhibit not only high mechanical strength but also superior separation performance [10–13].

Currently, Teflon AF2400 membranes reported in the literature have a membrane thickness in the micrometer range [6,9,14–16]. Such a large thickness is required in order to obtain defect-free membranes due to the use of macroporous supports, resulting in low gas permeance. Furthermore, Teflon AF2400 membranes were prepared on the supports with a low packing density (membrane surface area/ module volume ratio, m^2/m^3), such as disks and tubes, limiting the separation efficiency of membrane modules. Within the above context, these membrane devices are not sufficiently effective in practical separation of dissolved gasses from transformer oil for DGA.

In this study, we report the synthesis of ultrathin Teflon AF2400 membranes on modified macroporous alumina (Al_2O_3) hollow fiber supports. The Al_2O_3 support is used since it possesses not only strong mechanical strength but also high chemical and thermal stability, satisfying the requirement for oil-gas separation applications. Furthermore, compared with commercial porous ceramic tubes, Al_2O_3 hollow fibers with a small diameter have a lower gas transport resistance [17–20], enhancing the permeance of composite membranes. More importantly, hollow fibers feature a high-packing density ($> 1000\ m^2/m^3$) and cost-effective fabrication [21–23]. For the modification of support surface, the surface of the macroporous α-Al_2O_3 hollow fiber support is coated with a thin mesoporous γ-Al_2O_3 layer using the sol-gel method. Not only can this mesoporous layer effectively eliminate the surface imperfection of the α-Al_2O_3 support but also decrease the surface roughness [24,25], allowing synthesis of an ultrathin and defect-free Teflon AF2400 film on the support surface. The objective of this research study is to develop and report the synthesis and gas permeation performance of ultrathin Teflon AF2400/γ-Al_2O_3 composite hollow fiber membranes for the potential application as an extractor for DGA.

2. Experimental

2.1. Preparation of porous ceramic supports

Macroporous α-Al_2O_3 hollow fiber supports were fabricated by the phase-inversion and sintering method based on the research work by Tan et al. [26]. In this method, the hollow fiber precursor was obtained through spinning Al_2O_3 slurry which contains polyethersulfone (PES, Veradel A-301), N-methyl-2-pyrrolidone (NMP, 99.5%, Sigma-Aldrich), and polyvinylpyrrolidone (PVP, Sigma-Aldrich) as a binder, a solvent, and an additive, respectively. The macroporous Al_2O_3 hollow fiber supports were achieved by sintering the precursor at 1400 °C. The average pore diameter of the outer surface is about 200 nm, and the porosity is close to 60%. Macroporous α-Al_2O_3 disk supports were also prepared for the comparative study. α-Al_2O_3 power (A16, Sigma-Aldrich) was mixed with water and then pressed at 150 MPa to form green disks. After drying in a humidity-control oven, the disks were sintered at 1150 °C to form macroporous disk-type supports. The average pore diameter of the disk supports is about 200 nm, similar to that of the hollow fiber support.

To coat a γ-Al_2O_3 layer onto the macroporous Al_2O_3 supports, a boehmite sol was prepared using aluminum-tri-sec-butoxide (97%, Sigma-Aldrich) as a precursor, following the procedure reported by Hang et al. [27]. The boehmite gel-layer was formed on the outside surface of the hollow fiber supports or on one side of the disk supports by dip-coating. Subsequently, the coated supports were dried in a humidity-control oven (40% relative humidity) for 2 days and then calcined at 450 °C for 3 h in a furnace with a ramping rate of 0.5 °C/min.

2.2. Preparation of ceramic supported Teflon AF 2400 membranes

Teflon AF2400 solution of 1 wt% concentration (polymer molecular weight: 300,000–350,000; solvent: fully-fluorinated Fluorinert™ FC-770, Chemours™, Du Pont) was mixed with a predetermined amount of Fluorinert™ FC-770 ($C_{10}F_{22}$, Sigma-Aldrich) to form the solution with a desired concentration. Teflon AF2400 solutions of various concentrations (including 0.3, 0.4, 0.45 and 0.5 wt%) were coated onto the surface of the γ-Al_2O_3 layer of Al_2O_3 hollow fiber supports by the dip-coating method. For the preparation of Al_2O_3 disk supported Teflon AF2400 membranes, the 1 wt% Teflon AF2400 solution was used to coat onto one side of the disk. The as-prepared membrane was dried at room temperature for 1 day and then dried at 120 °C for 12 h to remove the residual solvent.

2.3. Membrane morphology characterization and single gas permeation measurement

The surface and cross-section morphology of supports and composite membranes were characterized using Scanning Electron Microscopy (SEM, Philips, XL 30). The single gas permeance through the composite membranes was measured at room temperature by the steady-state method in which the permeation rate under various transmembrane pressures was measured by a bubble flow meter. The gas permeance, in the unite of GPU [1GPU = 3.35×10^{-10} mol/(m^2 s Pa)] was calculated by Eq. (1):