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Carbon Whisker Membrane

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Abstract. We report a recent developed membrane called carbon whisker membrane (CWM). The CWMs consist of a tubular ceramic membrane covered by a layer of carbon film and carbon whiskers formed on the surface of the carbon film. Hydrocarbons such as methane and a modified chemical vapor deposition apparatus were employed for fabricating uniformed CWMs. Because of the unique feature of the CWMs, the filtration performance of the CWMs was investigated and it was found that the CWMs possess a function of anti-attachment of particles and/or biomaterials on the membranes so that the permeate flux and the cleaning process of the membrane can be improved.

Keywords: carbon whiskers, vapor grown carbon fibers, membrane separation

Introduction

Carbon whisker membrane (CWM) shown in Fig. 1 consists of a membrane substrate formed by the nucleation of ceramic granules, a layer of carbon coated film on the ceramic membrane and carbon whiskers (also called vapor grown carbon fibers, VGCFs) grown on the surface of the membrane. This novel membrane has recently developed in our laboratory (Li et al., 2000, 2001) and it is aiming to use it in the membrane filtration for preventing a rapid flux decline during filtration and for an easier membrane cleaning process. Carbon whiskers are expected to act as a secondary layer of the membrane to avoid particles and/or bio-materials blocking the pores of the membranes but attaching on the carbon whisker layer. As a consequence, the permeate flux can be improved and also generated cake layer can be removed easier by back flushing cleaning process. In this paper, we report the fabrication method of carbon whisker membrane by chemical vapor deposition methods with novel recipes and the application of the CWMs in the membrane filtration.

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Experimental

New recipes were found in our previous studies for the formation of vapor-grown carbon fibers (Li et al., 2000, 2001). They are ferric sulfate as catalyst precursor, nitrogen as carrier gas, methane as the source of carbon for the growth of VGCFs. 40 cm long tubular ceramic membranes with 13 mm O.D. and 2 mm wall thickness were firstly coated with ferric sulfate solution using dipping & coating technique and then dried at room temperature overnight. A modified chemical

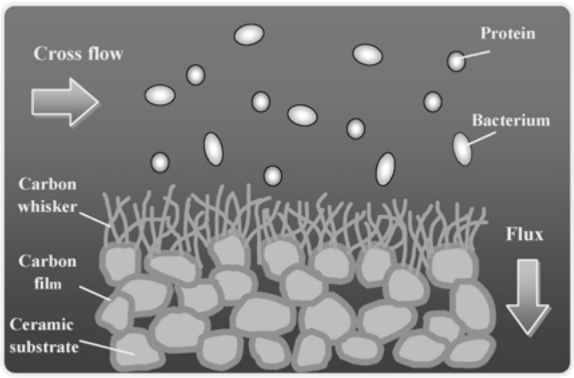
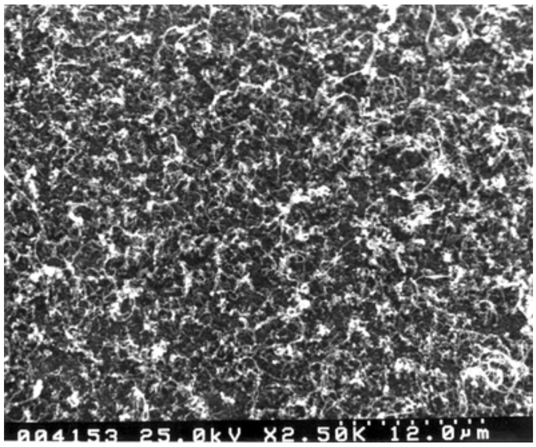
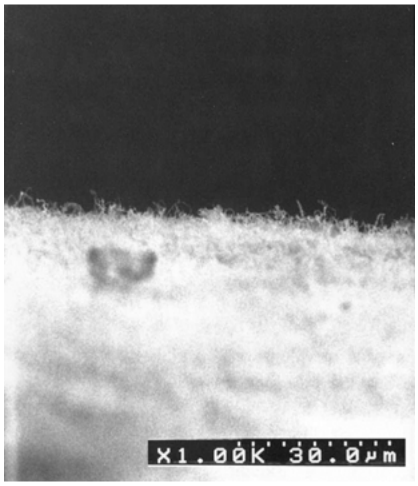


Figure 1. Carbon whisker membrane (CWM) and its applications.



(a)



(b)

Figure 2. (a) Top view of carbon whisker membrane under SEM observation. (b) Cross view of carbon whisker membrane under SEM observation.

vapor deposition apparatus (Li et al., 2002) which allows to reverse feed flow in the tubular reactor was employed for the fabrication. The tube was placed in the center of the reactor and then purged by nitrogen while the temperature raised to 1000 or 1100°C prior to the deposition of hydrocarbons. While the temperature reached to the steady state of a desired temperature, a gas mixture of 20% methane and 80% nitrogen with a flow rate of 500 ml/min was introduced into the reactor for a desired deposition time and reversed the direction of the methane flow periodically to ensure an unformed deposition.

Membrane filtrations were carried out with a cross flow membrane separation system. It consists of a cross flow membrane module, a feed pump, a recirculation pump and process pipes. The feed steam contained 1000 ppm PMMA with a mean particle size of 0.8 micrometer for the experiments. Backflushing technique to regenerate membrane was employed for one minute in every 20 min filtration process in order to remove attached particles.

Results and Discussions

Figure 2(a) and (b) shows the SEM observations of a top view and a cross view of the CWMs, respectively. As can be seen, carbon whiskers were randomly grown on the membrane with a high population density. The network-like whiskers acted as a secondary layer of the membrane. In the case of this CWM, the length and diameter of carbon whiskers are about a few micrometers and 0.1 micrometer, respectively while the thickness of carbon whisker layer is approximate 2 micrometers. The filtration performance of the carbon whisker membrane depends on the ability of trapping particles in the carbon whisker layer. If the size of the particles is much smaller than the gap of carbon whisker "network", the particles in feed stream will pass through the carbon whisker layer and block/attach on the pore of the membrane so that the filtration function of membrane decreases. Therefore, it is no doubt that the factors which determine the thickness and the gap size of the whisker network such as the population density, diameter and length of the carbon whiskers play an important role for the filtration performance of the carbon whisker membrane. By SEM observations of the CWMs, the characters of the carbon whiskers (length, diameter, population density) can be revealed.

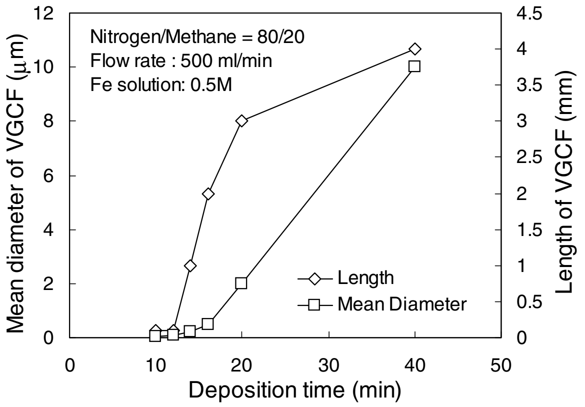


Figure 3. Length and diameter of carbon whisker versus of deposition time.

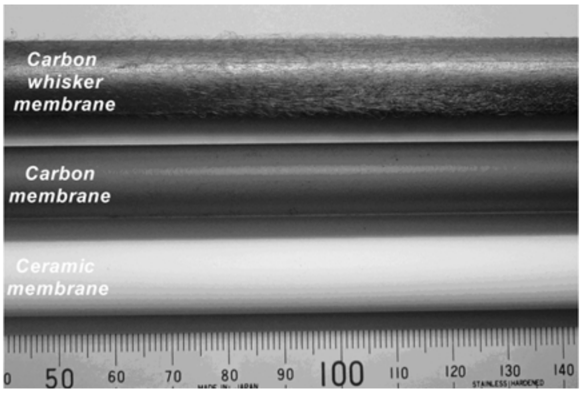


Figure 4. Carbon whisker membrane, carbon membrane and ceramic membrane.

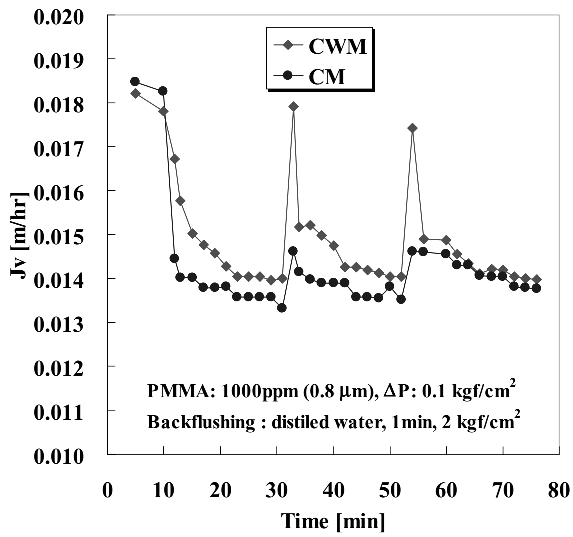


Figure 5. Flux versus time for crossflow membrane filtration with backflushing cleaning.

Figure 3 shows the length and diameter of carbon whisker versus the deposition time. As expected, the increase of deposition time led to increase the diameter and the length of the carbon whiskers simultaneously (Li et al., 2001). However, the lengthening of carbon whiskers is faster in the beginning of the growth stage while the diameter increased linearly. The maximum length and diameter of carbon whiskers can reach to a few millimeters and a few micrometers, respectively. By controlling the deposition time, flow rate, reaction temperature, the composition of the feed gases, it is possible to fabricate carbon whiskers with a desired diameter and length. For example, increasing reaction temperature will enhance the pyrolysis rate of the methane. This will speed up the deposition rate of the carbon species so that the growth rate of carbon whisker will therefore increase.

Figure 4 shows the three types of membranes, namely ceramic membrane (bottom), which was used as a substrate for the formation of carbon whisker membrane, carbon membrane (middle) (Li et al., 2001, 2002), which was fabricated by CVD of methane to modify the pore size of the ceramic membrane, and carbon whisker membrane (top). Uniformed membranes of 40 cm long with various pore sizes and whiskers in different diameter and length can be made by the CVD technique. In general, these membranes are for the use of ultrafiltration and nanofiltration. It also depends on the pore size of the membrane, the characteristics of the carbon whisker network. Carbon whisker membranes (CWM) and carbon membranes (CM) were firstly examined by pure water filtration to understand the water permeation ability. We selected the CWM and CM which had a similar flux of pure distilled water for the experiments of membrane filtration using PMMA solution. The purpose of the experiments was to compare both the performance of the water permeability and the flux enhancement by backflushing of distilled water. Figure 5 shows the results of the permeation experiments. As can be seen, after the input of PMMA solution, the flux declined rapidly in both carbon membrane and carbon whisker membrane. In comparison, flux decline in the carbon membrane is quicker than that of the carbon whisker membrane. This could be because the carbon whisker prevented

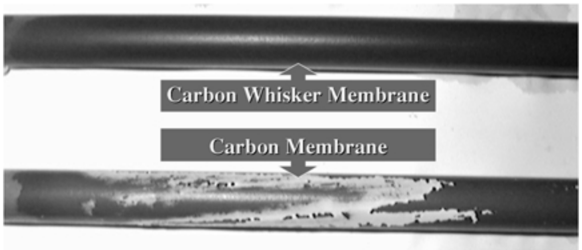


Figure 6. Observation of PMMA removal on membranes after backflushing cleaning procedure.

particles to attach and deposit on the pore of the membranes so that more water is capable to go through the membrane. After 20 min of filtration, the water permeation of membranes had reached its limit. Flux enhancement was then conducted with backflushing technique under a gauge pressure of 2 kgf/m^2 for one minute to remove the cake layer as well as particles deposited on the membranes. In contrast, the flux recovery on the CWM is higher than that on the CM. The results suggested that the CWMs possess an ability of anti-attachment of particulate matters due to the existence of the carbon whisker layer on the membrane. The particles were trapped on the whiskers layer rather than the membrane and, because of the flexible nature of the whiskers, it is easier to remove the particles from the whisker layer by the cleaning technique. After the backflusing cleaning of the membranes, the PMMA solution then continued to be fed to the module for the next filtration. The similar results were also found and shown in the second and third cycles of the filtration process. Figure 6 demonstrates the PMMA removal on membranes after backflushing cleaning procedure. It is obvious to see that PMMA particles can be removed easier from the surface of CWMs while a certain amount of PMMA particles still remained on the CM so that the flux can not be enhanced.

Conclusion

Carbon whisker membranes (CWMs) have been successfully fabricated with novel recipes by chemical vapor deposition. It consists of a layer of carbon whiskers on the carbon coated membrane. The primary crossflow filtration experiments were conducted to investigate the potential applications of carbon whisker membrane. We found that particles as a retentate on the filtration process can be trapped in the carbon whisker layer rather than attached on membrane body or blocked the pores of the membrane. As a result, the CWMs enabled to reduce the flux decline and also to assist the backflushing cleaning. The efficiency of the membrane usage is therefore enhanced.

References

Li, Y.Y., S.D. Bae, T. Nomura, A. Sakoda, and M. Suzuki, "Preparation of Custom-Tailored Carbon Whisker Membranes by Chemical Vapor Deposition," in *7th International Conference on Fundamentals of Adsorption*, May 20–25, Nagasaki, Japan, 2001 (in press).

Li, Y.Y., S.D. Bae, T. Nomura, A. Sakoda, and M. Suzuki, "Manufacture of Carbon Whisker Membranes for Bio-Separation, Eurocarbon 2000," in *1st World Conference on Carbon*, July 9–13, pp. 87–88, Berlin, Germany, 2000.

Li, Y.Y., S.D. Bae, A. Sakoda, and M. Suzuki, "Formation of Vapor Grown Carbon Fibers with Sulfuric Catalyst Precursors and Nitrogen as Carrier Gas," *Carbon*, **39**(1), 91–100 (2001).

Li, Y.Y., S.D. Bae, A. Sakoda, and M. Suzuki, "Fabrication and Characterization of Carbon Whisker," in *The 2nd Pacific Basin Conference on Adsorption Science and Technology*, May 14–18, pp. 376–380, Queensland, Australia, 2000.

Li, Y.Y., T. Nomura, A. Sakoda, and M. Suzuki, "Fabrication of Carbon Coated Ceramic Membranes by Pyrolysis of Methane Using a Modified Chemical Vapor Deposition Apparatus," *Journal of Membrane Science*, **197**, 23–35 (2002).

Li, Y.Y., A. Sakoda, and M. Suzuki, "A Review of Fabrication Methods of Carbon Membranes and Applications Related to Their Hydrophobic and Electrically Conductive Properties," *Journal of Institute of Industrial Science, University of Tokyo*, **53**(3), 70–74 (2001).